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A Symposium Held Under the
Auspices of the Analysis Instrumentation
Division of the Instrument Society of America
August, 1957

EDITED BY

VINCENT J. COATES
The Perkin-Elmer Corporation
Norwalk, Connecticut

HENRY J. NOEBELS
Beckman Instruments, Inc.
Fullerton, California

IRVING S. FAGERSON
University of Massachusetts
Amherst, Massachusetts

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FOREWORD

The following collection of papers represents the Proceedings of the Instrument Society of America's First International Symposium on Gas Chromatography. This was held at the Kellogg Center on the Michigan State University campus, August 28 through 30, 1957.

The Symposium was conceived in the Fall of 1956 in the course of a discussion among the chairmen of the various technical committees of the Analysis Instrumentation Division of ISA. These committees have as one of their important functions the responsibility of disseminating the latest detailed technical advances of analysis instrumentation, and promoting the application of these principles in industry. Many methods have been and are being used by these committees in their attempts to achieve this objective. An optimum, and perhaps obvious, manner of effecting this transfer of information, of course, would be to gather all interested people in one place for uninhibited free discussion. This, in effect, was the reasoning behind the initiation of these symposia: To effect the maximum interchange of information possible within the limitations of a large but intensely interested technical group.

A decidedly academic flavor was deliberately planned by scheduling morning and evening sessions. The afternoons were left open for recreation or free discussion. A rather unique method was designed to provide each man with the opportunity for unlimited discussion of differences of opinion, experimental observations, and direct questions. This was accomplished by charging each session chairman with the responsibility of generating as much discussion as possible following each paper. The controlled discussion was allowed to continue for five minutes. Following this period, and based on the participation and intensity of the discussion, a separate meeting room and afternoon starting time were assigned to allow the discussion to continue ad libitum. In this manner, everyone had an opportunity to present his detailed views in an uninhibited manner "from his own soap box."

The free discussion groups were very well attended; the spirited discussions, lasting from two to five hours, admirably attested to the success of the experiment. In many instances, observations and reports and bits of information only hours "old" were discussed. In the rapidly advancing field of gas chromatography, such information rapidly disseminated can save a great deal of duplicate time and effort.

Herein lies the basic reason for the existence of technical societies or meeting groups—stimulation of ideas through mutual contact, careful documentation in the form of technical papers, and selective dissemination of these papers and other pertinent technical information. The effectiveness of a technical society lies not only in the competence and initiative of its members, but also in the technical support of the advanced investigations in their respective fields. We are in high hopes that the ISA organization, and particularly the facilities of the Analysis Instrumentation Division, will continue to be recognized and utilized by all technical people interested in instrumentation.

We wish to express our thanks to the contributors, session chairmen, and many other people who have contributed to this effort. The assistance of Dr. J. D. Jackson, Dr. Lowell Eklund, and their staffs at the Kellogg Center is deeply appreciated. In particular, our greatest thanks go to Jean McDonald for her competent assistance to the General Chairman in handling the numerous details, correspondence, and arrangements necessary for the success of this operation.

HENRY J. NOEBELS, Beckman Instruments, Inc.

General Chairman,
International Symposium on Gas Chromatography

Associate Director,
Analysis Instrumentation Division

VINCENT J. COATES, The Perkin-Elmer Corporation

Program Chairman,
International Symposium on Gas Chromatography

Chairman,
Committee on Chromatography

IRVING S. FAGERSON, University of Massachusetts

Publication Committee,
International Symposium on Gas Chromatography

Member of Committee on Chromatography

THOMAS C. WHERRY, Phillips Petroleum Company

Director,
Analysis Instrumentation Division

LIST OF CONTRIBUTORS

B. O. Ayers, *Phillips Petroleum Company, Research and Development Department, Process Development Division, Bartlesville, Oklahoma*

W. J. Baker, *Monsanto Chemical Company, Plastics Division, Texas City, Texas*

Paul Benedek, *Hungarian Petroleum and Gas Research Institute, Veszprém, Hungary*

C. Eugene Bennett, *Polychemicals Department, E. I. du Pont de Nemours & Co., Inc., Du Pont Experimental Station, Wilmington, Delaware*

D. W. Carle, *Scientific Instrument Division, Beckman Instruments, Inc., Fullerton, California*

H. Newell Claudy, *The Perkin-Elmer Corporation, Norwalk, Connecticut*

C. B. Cowan, *Central Research Laboratory, Canadian Industries Limited, McMasterville, Quebec, Canada*

W. A. Dietz, *Esso Research and Engineering Co., Linden, New Jersey*

A. S. Dunlop, *Polymer Corporation Limited, Sarnia, Ontario, Canada*

Herman R. Felton, *Organic Chemicals Department, Jackson Laboratory, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware*

Marcel J. E. Golay, *The Perkin-Elmer Corporation, Norwalk, Connecticut*

J. C. Harden, *Polychemicals Department, E. I. du Pont de Nemours & Co., Inc., Du Pont Experimental Station, Wilmington, Delaware*

Lewis F. Hatch, *Department of Chemistry, The University of Texas, Austin, Texas*

Charles C. Helms, *The Perkin-Elmer Corporation, Norwalk, Connecticut*

E. A. Hinkle, *Monsanto Chemical Co., Texas City, Texas*

Theron Johns, *Beckman Instruments, Inc., Fullerton, California*

S. E. J. Johnsen, *Monsanto Chemical Co., Texas City, Texas*

J. J. Kirkland, *Grasselli Chemicals Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware*

Stanley H. Langer, *U. S. Bureau of Mines, Pittsburgh, Pennsylvania*

J. S. Lewis, *Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee*

A. J. P. Martin, *Abbotsbury, Barnet Lane Elstree, Herts., England*

R. A. Meyer, *Consolidated Electrodynamics Corp., Pasadena, California*[1]

J. L. Monkman, *Department of National Health and Welfare, Occupational Health Division, Ottawa, Ontario, Canada*

---

[1] Present Address: Atomics International Division of North American Aviation, Canoga Park, California

S. Dal Nogare, *Polychemicals Department, E. I. du Pont de Nemours & Co., Inc., Du Pont Experimental Station, Wilmington, Delaware*

Stanley D. Norem, *The Perkin-Elmer Corporation, Norwalk, Connecticut*

H. L. Norlin, *Monsanto Chemical Company, Plastics Division, Texas City, Texas*

Stephen S. Ober, *Abbot Laboratories, North Chicago, Illinois*

H. W. Patton, Research Laboratories, *Tennessee Eastman Company, Division of Eastman Kodak, Company, Kingsport, Tennessee*

C. Phillips, *Merton College, Oxford, England*

Russel D. Ring, *Wyandotte Chemicals Corporation, Wyandotte, Michigan*

Ralph E. Rippere, *General Engineering Laboratory, General Electric Company, Schenectady, N. Y.*

M. J. Root, *G. Barr & Co., Chicago, Illinois*

P. H. Stirling, *Central Research Laboratory, Canadian Industries Limited, McMasterville, Quebec, Canada*

Stephen Szépe, *Hungarian Petroleum and Gas Research Institute, Veszprém, Hungary*[2]

Leslie Szepesy, *Hungarian Petroleum and Gas Research Institute, Veszprém, Hungary*

B. W. Taylor, *Fisher Scientific Company, Pittsburgh, Pennsylvania*

G. W. Taylor, *Polymer Corporation Limited, Sarnia, Ontario, Canada*

R. F. Wall, *Monsanto Chemical Company, Plastics Division, Texas City, Texas*

J. F. Young, *Douglas Aircraft Co., Santa Monica, California*

Charles Zahn, *U. S. Bureau of Mines, Pittsburgh, Pennsylvania*

T. L. Zinn, *Monsanto Chemical Company, Plastics Division, Texas City, Texas*

[2] Present address: Sinclair Research Laboratories, Inc., Harvey, Illinois

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CHAPTER I

Theory and Practice of Gas-Liquid Partition Chromatography with Coated Capillaries

MARCEL J. E. GOLAY

The Perkin-Elmer Corporation, Norwalk, Connecticut

Few novel techniques have ever had as spectacular a growth as gas chromatography has had in the last few years, after a period of incubation of two decades. The manufacture of gas chromatographic instruments has mushroomed over a matter of months, and, a healthy sign, the propounding of theories of gas chromatography has also kept pace with the general interest awakened at last.

And so, you may well have said upon reading the title of my paper: What! Another theory?

The burden of proof is certainly on the one who has the temerity of bringing yet another brick to the structure already so carefully and competently built by Martin, Zuiderweg, Klinkenberg, Glueckauf, and Keulemans, to name but a few. Should this proof consist of showing another slightly different way of looking at the same phenomena? Or should a new theory bring a new viewpoint which suggests new experimental techniques? I shall let these questions rest with my readers and will proceed with what I want to say.

Not long ago[a] I used the communication engineering picture of Fig. 1 for a gas chromatographic column operated in the linear region. The upper row of condensers, moving with the velocity v, represents the moving phase. The lower row represents the fixed phase. Longitudinal diffusion within the moving phase is determined by the resistance, R, and diffusion between the two phases is determined by the conductance G. With this representation three things are shown readily: First, an injected sample acquires quickly a Gaussian density distribution; second, for maximum separation there is an optimum carrier gas velocity, v, which is determined by R, G, and the C's; and third, a formal expression for the HETP (height equivalent to a theoretical plate) can be given in terms of R and G.

The representation of Fig. 1 constitutes the basis for a mathematical theory of a chromatographic column. Such a mathematical theory is alright as far as it goes, because it leads to interesting qualitative conclusions. But what is really wanted is a physical theory which will give us a

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[a] American Chemical Society Meeting, Dallas, Texas, April, 1956.

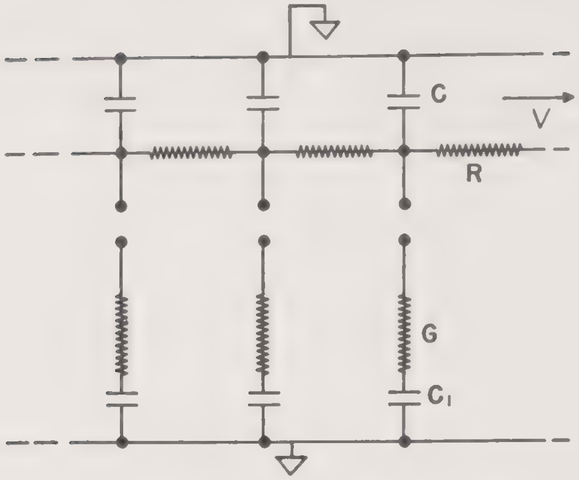

FIG. 1. Equivalent circuit of chromatographic column operated in the linear region

quantitative relationship between the performance of a gas chromatographic column, and such important experimental parameters as the analysis time and the carrier gas pressure which are required for a given performance.

Recently I made an initial stab at this problem by considering a packed Celite column as equivalent to a bundle of capillary tubes coated with a fixed phase, and with an inside diameter which was of the order of the granule size. Rough calculations indicated that the diameter of the capillaries which determines the resistance to gas flow, should also determine the order of magnitude of the HETP.

This embryonic physical theory had the remarkable property that it checked the experimental findings in every respect except one very important one: The Celite column behaved as if it were characterized by two granule sizes: A first granule size of the order of one mm, that is, ten times the actual Celite granules, determined the HETP. A second granule size of the order of 10 microns, 100 times smaller than the first, determined the resistance to carrier gas flow. This 100:1 ratio meant a viscous resistance to flow 10,000 times too great. It meant, for instance, that we were spending three hours for an analysis which should have required one second. In terms of relative component separation, it meant also that the resolution actually obtained had only one tenth the theoretically expected value, for given experimental conditions.

These tentative conclusions were the more puzzling because the bands of inert molecules, which I will call simply air peaks, were also ten times too broad. It followed that diffusion time within the oil patches, which had been ignored, could not be invoked to explain the discrepancy.

I was pondering over this when I happened to notice in the laboratory a rather long length of tygon tubing, and out of curiosity I substituted it for the Celite column, just to see what the air peaks would look like. I was pleasantly surprised to discover that these air peaks were of the correct width predicted by the same rough theory.

The next thought was: If the air peaks have the correct width when the column is a length of plain tubing, why not coat the inside wall of this tubing with a retentive substance, and use it for a partition column?

The answer to this question anticipates the second part of my talk, and before we go into this we first should do a little theoretical work, and establish an expression for the air peaks or the component peaks inside a coated capillary tube.

As you know, every linear theory of gas chromatography leads to the conclusion that the density distribution of any sharply injected component assumes a Gaussian shape of continuously increasing width as it progresses along a column. There may be circumstances external to the column itself which may upset this; for instance, a large injection volume, or a large detector volume, or a slow injection, or again a large time constant of the thermal detector, or even other causes, may produce exponential tailings. But a linearly operated column will always have density distributions which approach the Gaussian shape. This can be derived directly from the properties of a mathematical operation, called convolution, which plays such an important role in gas chromatography, that I should devote a few minutes to it.

Suppose that a gas packet is injected as a delta function at any point in the column. Its density distribution is represented by a sharp spike of area unity. Suppose that after traveling over a distance unity this spike has spread in the form of a rectangular function. Let now this gas packet travel a second distance equal to unity. Since we have assumed linearity, the principle of superposition applies, and we may decompose this rectangular distribution into a multiplicity of small spikes. After traveling another unit distance, each small spike will have its own secondary rectangular distribution, and the sum of these will be a triangular function, which represents the sample distribution after travelling two unit distances. The mathematical operation which produces a triangular function with two generating rectangular functions is called a convolution, and it has two properties which are of interest to us.

First if we keep repeating this operation several times, the resulting distribution will approach more and more the Gaussian shape, regardless of the particular shape of the primary distribution, which I happen to have taken as rectangular. It can be any distribution at all. Now the second property. Take any two distributions with their areas normalized to unity. Make their convolution: this gives you a third distribution, also of area unity; then take the second moment of each of these three distributions. This second moment can be pictured as the moment of inertia of the distribution area around its central axis. The second important property we shall use is this: the second moment of the resulting distribution is equal to the sum of the second moments of the two initial distribution. But "second moment" is an awkward expression for such a simple and important concept, and it will be more convenient to just adopt the word "spread" to designate this quantity. Thus the spread of several distributions convoluted with each other will be the sum of the individual spreads of each distribution.

With this simple convention, the total spread of a component travelling in a gas chromatographic column consists simply of the individual spreads contributed by every portion of that column.

Our next task will be to examine what happens when a component is being carried down a capillary tube coated with a layer of retentive oil or wax.

Fig. 2 shows a section taken through the middle of our capillary column. As gas flows through this column, the velocity distribution of the various gas portions is parabolic, but we can simplify the picture by assuming that the inner half of the gas cylinder flows at a uniform velocity $2\bar{V}$ while the outer half remains stationary. We have thus three phases, a fixed liquid phase on the wall, a fixed gas phase, and a moving gas phase.

We are now in a position to examine the two effects which operate to cause the spreading of small packets of air or of components having an affinity for the fixed liquid phase.

The first of these effects is easily visualized. It is due to the static diffusion of air or sample molecules in the carrier gas. In the time differential dt, the spread du caused by static diffusion is given by this simple expression:

$$du = 2D\,dt$$

where D designates the diffusion coefficient.

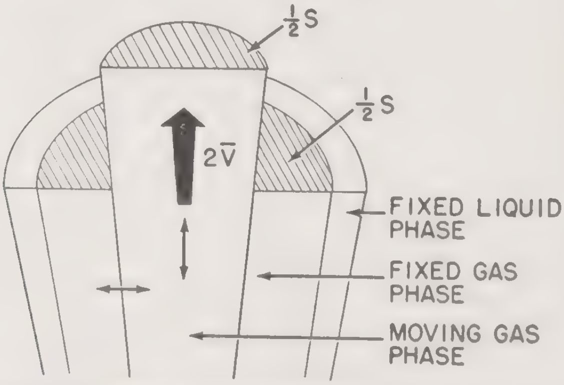

FIG. 2. Schematic section of coated tubular column.

This can be written also:

$$du = 2D \frac{S\,dx}{F}$$

where S is the capillary cross section, and F is the volumetric flow. The quantity $S\,dx/F$ is simply the time dt required for an air packet to travel the distance dx. This expression remains the same for packets of molecules having an affinity for the liquid phase because these molecules spend the same time in the gas phase as the air molecules, and their longitudinal diffusion in the liquid phase is negligible.

The second spreading effect is a little more difficult to visualize. Assume first that each air molecule spends exactly equal times in both the fixed and the moving gas phases. Then the total spread should indeed be given by the expression just written. But diffusion between these two phases is not instantaneous. The air molecule which happens to be somewhere in the moving phase will stay in it for some time, before it wanders into the fixed phase, where it will also stay some indeterminate time. The result of these indefinite times of occupancy of the two phases will be variations in the relative occupancy of both by the various individual air molecules, some lingering in the fixed phase, while others travel a little more than half the time in the moving phase. Thus, these variations will cause an additional spread. But here the effect of diffusion is the opposite from before, because a high diffusion constant will cause the various gas molecules to spend more nearly equal times in the two phases, and the resulting spread will be smaller. This effect is not nearly so simple to calculate as the first, but by making a few simplifying assumptions, I have derived for the spread due to this second effect the second term in the expression given below for du:

$$du = \left[2\,\frac{DS}{F} + .01\,\frac{F}{D}\right] dx.$$

You will note that the diffusion coefficient in this second term is now in the denominator, as we have just seen it should be. Also, the faster the flow F, the less the opportunity for equalized travel times in the two phases, hence F is in the numerator, as it should be. This expression is dimensionally correct, and the approximate numerical coefficient .01 is the part which requires a little work to obtain. I should like to propose an exact computation of this coefficient for tubes of various simple cross-sections as an important unsolved problem of gas kinetics.[a]

A last contribution must be added to our expression, which up to this point, is applicable to inert air molecules only. When molecules may be absorbed or adsorbed on the walls, we have an even greater opportunity for variations in the occupancy of the moving zone, and we need an additional term which I will also ask you to accept on faith and which completes our expression for du thus:[a]

---

[a] Dr. Martin indicated in his comments that this problem has been discussed by Geoffrey Taylor in the 3rd. vol. of the 1953 Series A Proceedings of the Royal Society.

$$du = \left[2\,\frac{DS}{F} + \left(.01 + .03\,\frac{C_1}{C + C_1}\right)\frac{F}{D}\right] dx.$$

When C_1, the fixed phase capacity, is zero, we have of course the expression we found for air molecules. For molecules having a high affinity for the liquid phase, C_1 is much larger than C and the variations in the occupancy of the moving zone are roughly four times as large. For these molecules the optimum flow F is half as large, and the overall spread is twice that for air.

It may be useful, at this point, to review what we have done, or not done, and to contrast this theory with former theories, and particularly with the theory of Zuidenweg and Klinkenberg.

First we note that the so-called eddy diffusion term is absent. Eddy diffusion is an unfortunate term at best for a process in which the Reynold's number is of the order of unity, and in which flow is decidedly viscous. At any rate, this term, which owes its origin to the anastomosis of a packed column, is not applicable to a single capillary.

Second, we note that the term due to the slowness of diffusion in oil is also absent. This is a more serious matter, and the essential reason for its absence is that, in principle, it is possible to reduce its effects by roughening or otherwise increasing the wall area, so as to decrease the thickness of the liquid phase, without increasing appreciably the access time of the gas molecules to all its portions.

In practice, the departure between ideal and actual performance will be ascribed to the absence of the oil diffusion term. This departure will also constitute a challenge to the ingenuity of the column designer, by showing him how much better he would be doing with a more dispersed liquid phase in a capillary column.

Most importantly we note the presence of the new double term due to finite sideways diffusion within the gas phase. The term "Ideal" has been applied, in the past, to columns in which, by magic, the same diffusion coefficient D was zero for the first term and infinite for the second term, in the parenthesis, but this constitutes a logical impossibility. These terms are the terms from which we cannot escape, while we may conceivably escape from the oil diffusion term, with a more suitable wall geometry for instance. There is even a hint that in Celite columns, the oil diffusion term is less important than this term, because the air peaks in Celite columns have the same relative width as the component bands.

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[a] See note at the end.

The most important thing to note about this expression is its quantitative character, and its sole dependence upon measurable physical quantities. This permits us to really come to grips with the problem. For instance, a simple transformation would show us that the optimum HETP is a quarter of the capillary diameter for air peaks, and one half of the capillary diameter for components where C_1 is appreciably greater than C, and this conclusion has been verified for the air peaks. But before talking about experimental results, we should transform this expression into a more practical formula. I will not take you through the steps of this transformation, because they are more laborious than illuminating. I will merely state that we can start from the relation just written, introduce the known resistance of a capillary to viscous flow, and eventually derive a relation between the viscosity of the carrier gas on the one hand, and experimentally observable quantities on the other.

For the assumed case of optimum flow rate, this relation is the following:

$$P.I. = \frac{\Delta t^4\, t_a}{t^3(t - \tfrac{3}{4}t_a)}\,\Delta p \cong 400\mu(=.08 \text{ poise for He}).$$

All the quantities in this expression are directly observable quantities; Δp is read on a pressure gauge and is expressed in dynes cm^{-2}. The elution time t, the air elution time t_a and the band width Δt are read off a chromatogram and are expressed in seconds. With He as carrier gas, they should combine to give us .08 poise if everything were perfect, and particularly if we had capillary columns in which diffusion time in the retentive layer were negligible. But everything is not perfect, and we may use this expression as a measure of the departure from perfection. I have called it the performance index of a column,[a] and its smallness is a measure of the goodness of the column. In principle it is independent of the column dimensions; it is a function of the packing material only if we have a packed column, for instance.

We can do something else with this expression. Let us rewrite it thus:

$$P.I. = \left(\frac{\Delta t}{t - t_a}\right)^4 \cdot \frac{(t - t_a)^4 t_a}{t^4(t - \tfrac{3}{4}t_a)} \cdot t\Delta p.$$

You see in the first term of the right member the fourth power of the relative band width. It is the quantity we desire most to keep small, in order to have maximum component separation. The second term is dimensionless. It has maximum value when t is approximately four times t_a. This indicates that a column will give us optimum performance when the capacity of the liquid phase is three times the capacity of the gas phase. And the last term, the product of the time of waiting times the pressure drop, is what you might call the price paid for a certain column performance. Written this way, the *P.I.* shows how waiting time and pressure may be traded for performance with a given column material

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[a] Nature, Aug. 30, 1957.

I should like to make it very clear that the *P.I.* is not proposed as a substitute for the number of theoretical plates. Written as you see it here, the *P.I.* is very nearly the product $t\Delta p$, which I have termed the price paid for a given performance, divided by the square of the number of theoretical plates.

We could compare the square of the number of theoretical plates to the horsepower of a motor, and we could also compare the *P.I.* to the rate of fuel consumption per unit horse power. Its smallness gives us a measure of the intrinsic goodness of a column, which can constitute the criterion on the basis of which a certain type of column is selected. After this initial selection has been made, the column can then be engineered to give us the maximum number of theoretical plates for a given available carrier gas pressure, and a given time of waiting.

And now we come to the core of the problem: How does the *P.I.* of real columns compare with the *P.I.* of ideal capillary columns?

The answers are rather challenging. For Celite packed columns the best *P.I.*'s for both air and components have been found to be of the order of 1,000, or four orders of magnitude worse than the theoretically expected value. This enormous ratio could be regarded as a measure of how much room for improvement there is.

But, as I told you before, the *P.I.* for air peaks was found to be of the order of the theoretical value.

And finally, the *P.I.* for coated capillary columns was found to be of the order of 10 for separated components.

It would thus appear that by going to coated capillary columns, we have achieved, about two of the four orders of magnitude improvement promised by the *P.I.* concept.

I would like to add something about the experimental aspect of the work done at Perkin-Elmer, and also present a few results, and speculate on likely directions of future developments.

After the original test with tygon tubing showed a good behavior of the air peaks, a one meter length of glass capillary tubing, .032″ i.d. was coated with polyethylene glycol and showed a bare separation of components. This was significant nevertheless, because a very encouraging value was calculated for the performance index. This was followed by some experi-

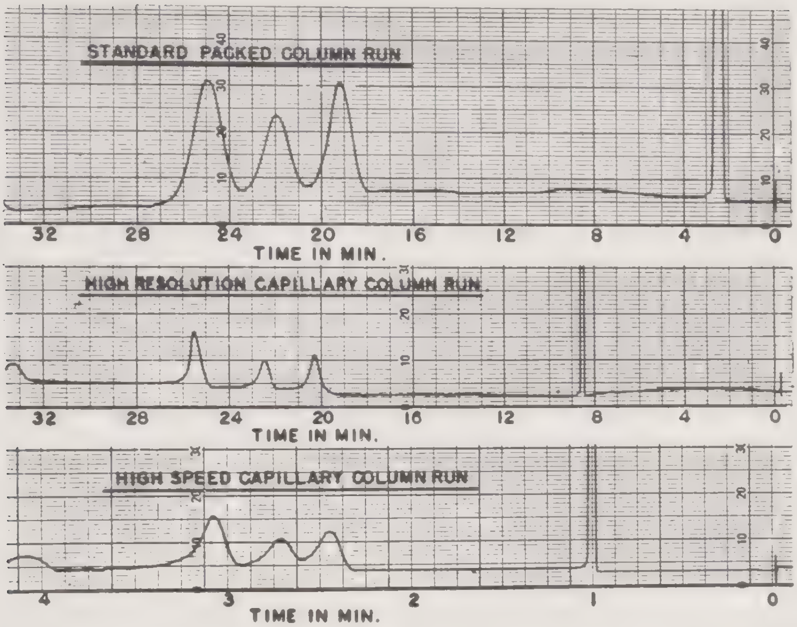

FIG. 3. Comparative results obtained with regular and capillary columns.

mentation with stainless steel tubings, .055″ i.d. which were coated by the simple process of swabbing them with a 10% mixture of polyethelene glycol in chloroform, and then letting the chloroform evaporate. Finally, relatively long lengths of stainless steel, and later copper tubing were acquired, most of which were .010″ i.d. The swabbing method was obviously unsuited to coat these, and a new and very effective coating method was developed. It consists in simply filling appropriate lengths of capillary with a 1% solution of polyethelene glycol in methyl chloride, closing off one end, and moving the open end slowly into an oven heated at 100°C. As the solvent evaporates, it leaves a thin coating of glycol on the inside wall of the capillary tubing.

Figure 3 illustrates comparative results obtained with a standard 4 m packed column, a 300′ capillary column, and a 100′ capillary column, all operated at 30 psi. The times required for the run are as shown. The number of theoretical plates calculated from the width at mid-height of the third component were 1700 for the standard column, 12000 for the first capillary column, and 2500 for the second capillary column.

As matters stand now, the most important problem to be solved for tubular columns is the reduction of the diffusion time in the retentive layer, relative to the diffusion time in the carrier gas. Two general attacks on this problem can be considered.

The first consists in increasing the wall area, without unduly increasing the access time to all parts of this area, and also without reducing appreciably the free bore of the capillary, which determines the resistance to carrier gas flow. Ideally, we would like a velvet lined capillary, or one with an inside wall covered with a log jam of dentritic particles. I am inclined to think that this solution is more difficult than it may sound, because of the effect of surface tension in causing the oil to accumulate at the cross-over points of this log jam.

The second solution consists in leaving the walls as they are, and in increasing the diffusion time in the carrier gas. The possibility of a heavier carrier gas does not look attractive. But the use of a high inlet pressure looks very attractive because our expression for the *P.I.* indicates that higher pressures can be traded for faster operation or increased resolution, and thus a double benefit could be derived from high pressure operation. The one drawback of this procedure concerns the low vapor pressure of the high boilers. Injection of these samples at a higher pressure means a proportionately decreased density at the column outlet, and this in turn places a higher burden on detector sensitivity.

Note

In the expression giving du, the quantity within the bracket is the HETP when the number of plates is defined phenomenologically as $8lg_e2$ times the square of the ratio of the passage time over the bandwidth at mid-height.

On the other hand, if the HETP is defined as the column length over which, in order to reproduce the observed spread, the mobile and fixed capacity may be lumped, with instantaneous equilibrium being realized every time the mobile phase advances suddenly one HETP, then the quantity within the bracket must be multiplied by $C_1/C + C_1$ to yield the HETP.

It must be noted that this latter definition of the HETP, more physical than the first because it is based on an idealization of the processes occurring in actual multi-plate distillation columns, leads to difficulties when C_1 becomes zero in either a Celite packed column or in a capillary column. The concept may then be restored to existence by considering a flowing gas mass within a capillary as consisting of a mobile and a fixed phase, but different answers are obtained depending upon what fraction of the gas mass is assigned arbitrarily to a mobile phase, and what fraction to a fixed phase.

It is because of these conceptual difficulties which appear when C_1 ceases to be much larger than C that expressions for the "spread" have been obtained directly, without recourse to any strict HETP concept, albeit the HETP, defined phenomenologically as noted above, has at least colloquial usefulness, when discussing column performance.

It should be noted also that the number of theoretical plates, likewise defined, is a measure of what separation a column is trying to achieve, and will achieve in the usual packed columns, but may be far from achieving in any column in which there is but little partition in the fixed phase.

Acknowledgment

The writer is indebted to Drs. Martin and Keulemans and to Mr. Jones of du Pont for a stimulating discussion of these important concepts.

Discussion

SKARSTROM (*Esso Research and Engineering Company, New Jersey*): Why couldn't you turn the capillaries inside out, coat thin wires, and bundle them?

GOLAY: If you just bundle them without leaving a hole in the center, you would have roughly the equivalent of a capillary which you have partially crimped; that would be the equivalent of several capillaries used in parallel. I do not believe a big improvement would be obtained from that. On the other hand, if you could somehow have the lining of the walls made up of many capillaries, thus increasing the area without increasing the access time to various parts of it, I believe you would have a real improvement. But the problem is a mechanical one. How would you do it?

MARTIN (*England*): First of all, I would like to congratulate you, Dr. Golay. I have been thinking on exactly the same lines as this and you've beaten me to it—very thoroughly. I would like to ask you how far you think your expression and your coefficients will change if you do not consider the center part of the gas moving and the outer part fixed, or at least if you consider the gas moving at two different speeds? Taylor, in a paper in the Proceedings of the Royal Society of a few years ago, has worked out the diffusion case which corresponds to your air case for a parabolic distribution of velocities. I wondered if you have compared the coefficients he derived from his work with the coefficients which you have derived.

GOLAY: I confess I did not know of that work, and I wish that I had because it would have saved me some work. I am looking forward to obtaining your reference in order that I might see how the two compare. It is quite possible that his is much more accurate than mine. Perhaps you can tell me if his analysis is completely rigorous, or is also made up of approximations.

MARTIN: I think his is quite rigorous within a certain range of flow rates. He gives the limits of flow rate over which his expression can be expected to hold rigorously. His work, of course, does not include any term which would correspond to the oil film on the side of the tube.

GOLAY: No, of course the term corresponding to the oil film is $.03\ C_1/C + C_1$. Now I should guess that if his expression is accurate it would be accurate over any flow rate so long as the Reynolds number is small enough to give us viscous flow, which is, of course, of the order of less than a thousand.

MARTIN: No, I don't believe so. His expression will only hold when the bands are sufficiently diffuse so that you can assume practically linear conditions over a short length of tube. If you consider the initial portion when the peak is infinitely high, then I think this expression will no longer hold. This is of no practical significance, however. But from a mathematical point of view, I believe, the expression will only hold over a certain range of flows.

GOLAY: It should hold, I would guess, after an infinite time of waiting in theory, but after a very short time in practice, as soon as the distribution is a Gaussian one, and it should be good, I would guess, for any flow rate which is viscous.

MARTIN: Well, I think it will be good under all practical conditions. But I believe there is a theoretical limitation here.

GOLAY: Well, in this case, what I have indicated as being an unsolved problem turns out to be a solved problem.

MARTIN: It's not, of course, in the same dress as yours. These results will have to be turned around a little to obtain the same expression. The mathematics, however, should be the same.

ANONYMOUS: Dr. Golay, what do you think the effect would be of using a shorter column with larger diameter, having the columns rotating so that you might have centrifugal forces coming into play?

GOLAY: I cannot guess at that, but as soon as you speak of centrifugal forces, I would suspect nonlinearity. My remarks apply to strictly linear conditions. I should add that the eddy diffusion term may have been the source of some confusion. Perhaps this was not too clearly shown.

RITZENTHALER (*Standard Oil Company, Indiana*): Dr. Golay, in your expression for the performance index, is that expression independent of pressure, or what is the range of pressures over which this would hold true?

GOLAY: For very high pressures, this should theoretically hold tuue, except for the coefficient of 16/27, by which you should multiply. In short, it is independent of the pressure range.

KEULEMANS (*Koninklijke/Shell-Laboratorium, Amsterdam, Holland*): In regard to the term eddy diffusion, which certainly has given rise to some confusion, I should like to remark that Klinkenberg and others never meant it to be interpreted as being true eddy diffusion, but as an analogy. I believe they always put the term eddy diffusion between inverted commas or quotation marks. It can be treated, however, mathematically in the same way as true eddy diffusion, but it never has been meant as a true eddy diffusion. They were certainly aware that this could not have occurred at these low Reynolds numbers.

GOLAY: Do you mean to say that in a column of which the Reynolds number is of the order of unity we may have true eddies?

KEULEMANS: No, there are no true eddies. However, this, if treated mathematically the same way as eddy diffusion is treated, can be compared, to a certain extent, with the phenomena of true eddy diffusion. Perhaps the name of the term has not been very happily chosen. I personally was not too happy with this nomenclature.

GOLAY: Yes, the term is not too happy a one. Regardless of the name, I agree it is a term which has its place in a packed column because of anastomosis, the possibility of different paths in and about the packing particles. This, of course, should not occur in a capillary.

DAL NOGARE (*E. I. du Pont de Nemours & Co., Inc., Delaware*): I notice your expression of the oil diffusion term. This means that you agree with the Jones and Keiselbach theory that the viscosity of a liquid phase plays no part in the spreading of these peaks?

GOLAY: No, it doesn't mean that. I *wish* it played no part. I hope that the future development might make it play no part by cutting down the thickness of the oil phase so as to reduce the diffusion time. You see, I cannot get away from diffusion in air because the very same term which gives me what I *don't* want in the longitudinal direction gives me what I *do* want in the cross-sectional direction. But of course this is all one world and I have to take the good with the bad and optimize my expression. In theory, I can do something with the oil diffusion term by making the walls ideally like velvet. If I could have a seriated wall, and if I could coat these little seriated projections uniformly with the oil phase, I would have something similar to an idealized column.

DAL NOGARE: Would you like to speculate as to what would be the effect of having a mono-molecular oil layer?

GOLAY: I would guess that as soon as you have a mono-molecular, you would have, in effect, the same as adsorption, rather than absorption. Then you no longer worry about this oil diffusion term. But then, of course, you worry about the nonlinearity of your isotherms because you have reduced terrifically your linear range of operation. You are back in the notoriously nonlinear adsorption column.

MARTIN: I would like to make this a triangular argument with Dr. Keulemans. I say I agree with Dr. Golay that the eddy diffusion term is probably not a real one. It seems to me that the crucial difference is whether or not there is a term that is not flow dependent. I myself think that it is improbable that there is any term which is not flow dependent. Would you agree with that, Dr. Golay?

GOLAY: I am quite sure that there is none in a capillary column, and I must confess that I have not thought it out completely in a packed column where you have a terrific amount of anastomosis.

JONES (*E. I. du Pont de Nemours & Co., Inc., Delaware*): I have one or two comments with regard to the so-called Jones, Keiselbach theory. We have looked into this eddy diffusion term and have found it to be a function of the pressure of the carrier gas, and of the diffusivity of the carrier gas as well. We also have some ideas on the Klinkenberg, Keulemans, van Deempter equations.

CHAPTER II

A Derivation of the Equation for Elution Chromatography Assuming Linear Rate Constants

J. F. YOUNG

Douglas Aircraft Co., Santa Monica, California

Since the advent of elution chromatography, a large number of empirical relationships have been established. Most attempts to correlate these relationships with fundamental thermodynamic constants have been relatively unsuccessful. In the case of frontal displacement chromatography, there has been some success (*1–3*), but in elution chromatography most analyses are based on a "theoretical plate" concept (*4*) which involves a number of empirically determined constants.

The "theoretical plate" concept is based on an assumption of equilibrium between the components in the liquid on the plate and those in the vapor. This condition is probably not even approached on the chromatographic column. In addition, peaks more closely approach the ideal when the ratio of sample material to column material is very low.

This latter fact suggests that the process taking place on the column is essentially a linear one, since most adsorption isotherms approach linearity as the amount of adsorbed material becomes very small. A linear process can also be inferred from the essential facts concerning elution chromatography. The fact that one obtains a definite retention time relatively independent of quantity and, under certain conditions, constant peak forms would indicate a linear process.

There has been some work done based on the assumption of a linear process in the chromatographic column (*5–7*). The reported work (*5*, *6*) however, gives no concise interpertation of the coefficients in terms of the parameters encountered in gas chromatography.

In the following derivation, we will assume that the moles per second adsorbed is equal to the rate constant k_a multiplied by the concentration and by the area dA with which the mixture is in contact. The probability per unit time that the substance will be desorbed is equal to a constant, k_d.

A = Total surface area of column.
$q(x, t)$ = no. of moles per sec. flowing past point x.
R = rate of flow in cc/sec.
$C = q(x, t)/R$ = concentration in moles/cm^3.

Q = La Place transform of $q(x, t)$.
L = Length of column.

$$q \rightarrow \underset{dx}{\Big\|} \rightarrow q + \frac{\partial q}{\partial x}\,dx$$

Consider the flow through an element of column dx. An amount will be adsorbed proportional to the elementary area and to the concentration.

$$dq \text{ (adsorbed)} = \frac{\alpha q\,dx}{L}, \qquad \text{where } \frac{k_a A}{R} = \alpha$$

An amount will be desorbed proportional to the amount of material on the elementary column area.

$$k_d \int_0^t - \frac{\partial q}{\partial x}\,dx\,dt.$$

Combining these we obtain:

$$\frac{\partial q}{\partial x} = -\frac{\alpha q}{L} - k_d \int_0^t \frac{\partial q}{\partial x}\,dt. \tag{1}$$

Taking the La Place transform:

$$\frac{\partial Q}{\partial x} = -\frac{\alpha Q}{L} - \frac{k_d}{S}\frac{\partial Q}{\partial x} \tag{2}$$

and,

$$Q = K^{\frac{(\alpha_m S)}{S+k_d}} \tag{3}$$

where $\alpha_m = \int_0^L \alpha \dfrac{dx}{L}$ and K is a constant.

The simplest form of this equation will be realized when the input to the column is an impulse function, i.e.,

$$q(0, t) = K u_1(t)$$

$$K = \int_0^\infty q\,dt.$$

K is then equal to the total number of moles introduced into the column, a constant.

The inverse transform of this equation and hence the equation for variation of concentration with time of a chromatographic column is

$$q = K e^{-\alpha_m}\left[u_1(t) + \sqrt{\frac{\alpha_m k_d}{t}}\, e^{-k_d t} I_1(2\sqrt{\alpha_m k_d t})\right]. \tag{4}$$

Where I_1 is the first order modified Bessel function, $u_1(t)$ is the unit impulse function and merely represents the original input unchanged except for being reduced by a factor of e. Since α_m is on the order of one hundred or greater, this term is negligible and for all practical purposes our equation may be written

$$q = Ke^{-(\alpha_m + k_d t)} \sqrt{\frac{\alpha_m k_d}{t}}\, I_1(2\sqrt{\alpha_m k_d t}). \tag{5}$$

It can be shown with the proper substitution of parameters that this equation is the same as equation (10) of reference (*6*).

To obtain our equation in terms of concentration, we divide by R and obtain

$$C_0 = \frac{K}{R_0}\, e^{-(\alpha_m + k_d t)} \sqrt{\frac{\alpha_m k_d}{t}}\, I_1(2\sqrt{\alpha_m k_d t}). \tag{6}$$

The area under the curve at the exit of the column is equal to

$$\int_0^\infty C_0\, dt = \int_0^\infty \frac{q\, dt}{R_0} = \frac{K}{R_0}$$

so we will designate this area by a new constant K_0 ; then

$$C = K_0 e^{-\alpha} \alpha k_d \left[\frac{e^{-1/2\alpha k_d t}}{\sqrt{\alpha k_d t}}\, I_1(2\sqrt{\alpha k_d t}) \right]. \tag{7}$$

Setting $\alpha k_d t$ equal to a new variable x

$$C = K_0 e^{-\alpha} \alpha k_d \left[\frac{e^{-x/\alpha}}{\sqrt{x}}\, I_1(2\sqrt{x}) \right] \tag{8}$$

$$\begin{aligned} \frac{dC}{dx} = K_0 e^{-\alpha} \alpha k_d \Biggl\{ \left[-\frac{1/\alpha\, e^{-x/\alpha}}{\sqrt{x}} - \frac{\frac{1}{2} e^{-x/\alpha}}{x^{3/2}} \right] I_1(2\sqrt{x}) + \frac{e^{-x/\alpha}}{\sqrt{x}}\, I_0(2\sqrt{x}) \\ + \frac{e^{-x/\alpha}}{2\sqrt{x}}\, I_1(2\sqrt{x}) \Biggr\}. \end{aligned} \tag{9}$$

Maximizing by equating to zero

$$\frac{1}{\alpha} + \frac{1}{2x} = \frac{1}{\sqrt{x}} \frac{I_0(2\sqrt{x})}{I_1(2\sqrt{x})} - \frac{1}{2x} \tag{10}$$

$$\alpha k_d t_r = x = \alpha \left[\frac{I_0(2\sqrt{x})}{I_1(2\sqrt{x})} \sqrt{x} - 1 \right] \tag{11}$$

$$k_d t_r = \frac{I_0(2\sqrt{x})}{I_1(2\sqrt{x})} \sqrt{x} - 1, \tag{12}$$

where t_r is the retention time since it occurs at the maximum value of C.

As the value of the argument for the modified Bessel function becomes very large

$$\frac{I_0(2\sqrt{x})}{I_1(2\sqrt{x})} = 1$$

$$k_d t_r \approx \sqrt{x} = \sqrt{\alpha k_d t_r} \tag{13}$$

therefore

$$\alpha \approx k_d t_r$$

and substituting in eq. 7

$$C_{\text{max.}} \approx \frac{K_0}{2}\sqrt{\frac{\alpha_m}{\pi}}\,\frac{1}{t_r} \tag{14}$$

$$\frac{t_r}{k_0/C_{\text{max.}}} \approx \frac{1}{2}\sqrt{\frac{\alpha_m}{\pi}}\,. \tag{15}$$

The value K_0/C_{max} is the value of the conventional "half-width" of the chromatographic curve so we will designate it Δt_r ; $t_r/\Delta t_r$ is a measure of the resolution.

Since α_m is directly proportional to the column length, this yields the known empirical fact that the resolution is approximately proportional to the square root of the column length.

The constant α is also inversely proportional to the velocity, so resolution should be inversely proportional to the square root of the velocity, and the retention time should be inversely proportional to the velocity. None of the references given give this relationship between resolution and flow rate, but reference (*8*) does state that the retention volume (i.e. Rt_r) was found to be constant over a wide range of values for flow rate.

Due to the apparent discrepancy in the theory, measurements of resolution and retention time were made at different rates of flow. These runs were made on a Perkin-Elmer Model 154 Vapor Fractometer using a two meter ¼ inch diameter stainless steel column packed with 40–80 mesh Linde Molecular Sieve #5A.

In order to determine the effect of changing velocity in the column, we must evaluate

$$\alpha_m = \frac{Ak_d}{L}\int_0^L \frac{dx}{R}\,.$$

The rate of flow will vary through a column due to the varying pressure

$$R = \frac{p_0}{p}\,R_0\,,$$

where R_0 and p_0 are the flow rate and pressure at the exit of the column and by Poiseuille's law

$$\frac{dp}{dx} = K_2R.$$

Then

$$p\,dp = K_2p_0R_0\,dx \qquad dx = \frac{p\,dp}{K_2p_0R_0}$$

$$L = \int_{p_i}^{p_0} \frac{p\,dp}{K_2p_0R_0} = \frac{(p_i^2 - p_0^2)}{2K_2p_0R_0}\; K_2 = \frac{(p_i^2 - p_0^2)}{2Lp_0R_0}$$

$$\begin{aligned}\alpha &= \frac{Ak_d}{L}\int_0^L \frac{dx}{R}\\ &= 2Ak_d\left[\frac{p_0^2R_0^2}{p_i^2 - p_0^2}\right]\int_{R_i}^{R_0}\frac{dr}{R^4}\\ &= \frac{2}{3}Ak_d\left[\frac{p_0^2R_0^2}{p_i^2 - p_0^2}\right]\left[\frac{1}{R_0^3} - \frac{1}{R_i^3}\right]\\ &= \frac{2}{3}\frac{Ak_d}{R_0}\frac{p_i^3 - p_0^3}{p_i^2 - p_0^2}.\end{aligned}$$

Since Ak_d/R_0 is the value α would have at constant flow, we will refer to it as α_0 and since

$$\frac{2(p_i^3 - p_0^3)}{3(p_i^2 - p_0^2)}$$

is the mean column pressure p_m then $R_m = R_0\,\dfrac{p_m}{p_0}$.

The values shown in Table I indicate that the resolution increases with decreasing flow rate but that it probably reaches an asymptotic value. The next to last column gives an indication of the conformance of the resolution to the equation which was derived.

TABLE I

R_0	p_i	p_m	R_m	t_r	$\frac{t_r}{\Delta t}$	$R_m\left(\frac{t_r}{\Delta t}\right)^2 \times 10^{-1}$	R_mt_r
118	34.7	26.0	67	4.7	4.6	1.4	315
70.5	29.7	23.5	44	6.4	5.1	1.1	280
52.4	26.7	21.3	36	8.6	5.5	1.1	310
35.9	23.7	19.6	27	12.2	6.1	1.0	330
20.0	20.7	17.8	16.5	18.0	6.3	0.7	320

The failure of the equation to predict accurately the change in resolution with flow rate is probably due to diffusion of the front or loss of linearity. The conformance of the retention time is good, as indicated by the last column of the table.

It can be shown that slight deviation from linearity of the adsorption should result in no shift in the retention time for a vapor. The chromatographic process can be thought of as a summation of linear processes, i.e.,

$$C_0(t) = \sum_n K_{0,n} e^{-(\alpha_n + k_{d,n} t)} \sqrt{\frac{\alpha_n k_{d,n}}{t}} \, I_1(2\sqrt{\alpha_n k_{d,n} t}).$$

The linear portion of the isotherm will be the only portion exhibiting a discrete retention time, hence the contribution of the rest should do little but broaden the curve.

Due to this relative invariance of retention volume of a substance on a column, it should be worthwhile to examine its theoretical significance.

Under equilibrium conditions, the amount of vapor being adsorbed is equal to that being desorbed, i.e.,

$$k_a A C_v = k_d m_s ,$$

where C_v and m_s are the concentration in moles per ml. in the vapor and the moles adsorbed on the solid respectively. Then

$$\frac{k_a}{k_d} A = \frac{m_s}{C_v}$$

but by eq. (13) $\alpha / k_d = t_r$

$$k_a = \frac{R}{A} \alpha \qquad \alpha = \frac{A k_a}{R} \qquad R t_r = \frac{k_a}{k_d} A = \frac{m_s}{C_v} .$$

Rt_r is the retention volume and is equal to $\frac{m_s}{C_v}$, the slope of the adsorption isotherm.

It should be possible to obtain the heat of adsorption from the value of the retention volume of a substance at two different temperatures.

By the Clausius Clapeyron Equation,

$$ln \frac{p_1}{p_2} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

The equilibrium pressure at constant m_s will be inversely proportional to V_r , the retention volume, so

$$ln \left(\frac{Vr_2}{Vr_1} \right) = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

from which ΔH can be calculated.

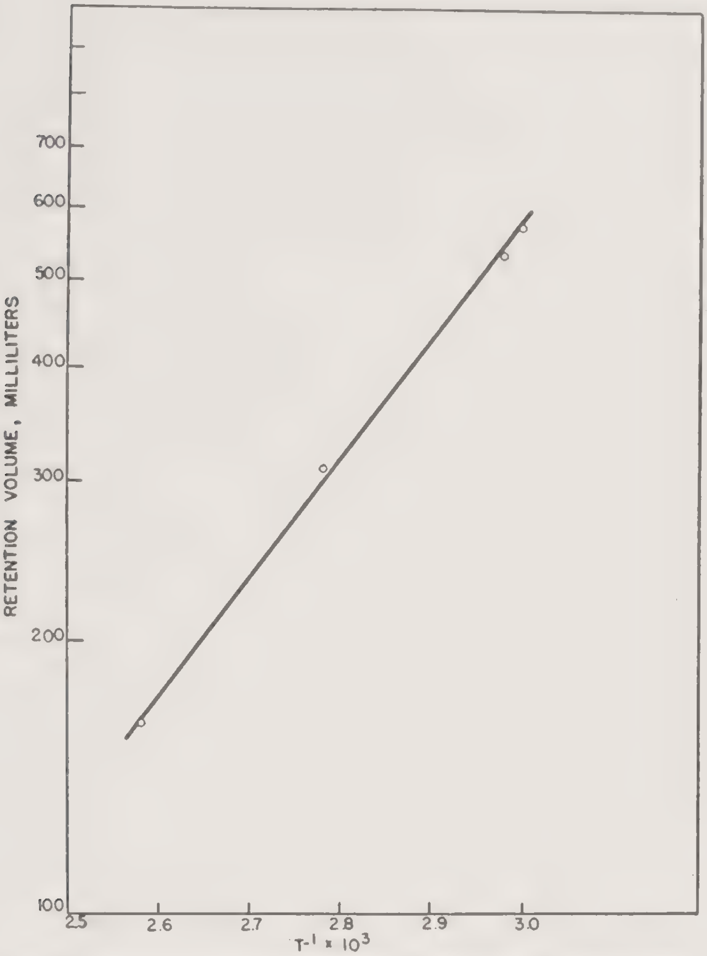

FIG. 1. Retention volume versus reciprocal temperature.

Essentially the same reasoning will apply for a GLPC column. In Fig. 1, the log of V_r is plotted against the reciprocal of the temperature for heptane on a Perkin-Elmer Column A. The slope is multiplied by 2.3 to change to log base e and equated to $\Delta H/R$. This yields a molal heat of vaporization of 6000 calories for heptane from the material of Column A. The molal heat of vaporization of heptane is approximately 7000 calories, so this is a reasonable figure.

In order to actually evaluate the meaning of the retention volume for a liquid partition column, we must go back to our original expression for the rate of desorption. With a liquid we have the same condition as in the flowing gas and all of the adsorbed material is not on the surface so we must introduce an area term as for adsorption, i.e. A_l/V_l. Then our expression for rate of desorption will be

$$k_d \frac{A_l}{V_l} \int_0^t - \frac{\partial g}{\partial x} \, dx \, dt,$$

where A_l and V_l are the surface area and volume, respectively, of the stationary liquid.

We must then multiply k_d by A_l/V_l in our equation for Rt_r,

$$Rt_r = \frac{k_a A}{k_d A/V_l} = \frac{k_a}{k_d} V_l$$

$$\frac{Rt_r}{V_l} = \frac{k_a}{k_d}.$$

This equation indicates that the retention volume per unit volume of stationary phase component, which we will designate the "specific retentivity," is a constant proportional to the Henry's Law constant for the vapor in the stationary phase.

If we designate the retention volume per mole of stationary liquid the molal retentivity it can be shown that the gas constant, R, times the absolute temperature divided by the molal retentivity is equal to the slope of the partial pressure versus molal concentration curve, i.e.,

$$p_0 = \frac{RT}{\rho}$$

$$p = p_0 m$$

where

ρ = molal retentivity
R = gas constant
p = partial pressure above stationary phase
m = molal concentration of vapor in stationary phase.

In order to test the validity of this concept, Johns Mansville C-22 fire brick was mixed with two different amounts of tricresyl phosphate and packed in a 110 cm column. The retention time of methylene chloride was

TABLE II

Column	No. 1	No. 2
Wt. TCP.	1.74 gm	3.26 gm
t_r	4.9	10.6
R	26.0	23.2
Pressure	2 psi	2 psi
V_r	1.34	2.53
ρ (liters/mole)	28.0	28.3
Δt	0.5	1.4
$t_r/\Delta t$	9.8	7.4

measured on both of these columns at 59°C. with the results indicated in Table II.

The constancy of the value for specific retentivity indicates that diffusion into the liquid phase is a very small factor at least for the case of dichloromethane on TCP. The diffusion may result in a slight loss of linearity as manifested by the decrease in resolution with increase in volume of the stationary phase.

A subsequent search of the literature revealed that the concept of retention volume per unit volume of the liquid phase is not new. Littlewood (*9*) gives values for various combinations of vapors and stationary phases. In addition, he gives a relationship between the specific retentivity and the partition coefficient. No derivation is given for this relationship; however, it can be shown to be identical to the relationship derived in this paper. The pressure drop correction is also the same as that derived here and is credited to Martin and James (*10*).

More recently, Pollard and Hardy (*11*) have published values of retention volumes per gram and heats of vaporization for halogenated hydrocarbons.

It is felt that prediction of resolution can be just as successful as that of retention time with a further study into the variables affecting diffusion of a vapor front through a column.

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CHAPTER III

An Empirical Method for Converting Gas Chromatographic Elution Areas to Concentrations

E. A. HINKLE AND S. E. J. JOHNSEN

Monsanto Chemical Co., Texas City, Texas

The quantitative analysis of complex mixtures by gas chromatography would be quite simple if the elution area of a component were a direct measure of the number of moles of that component in the mixture. This is not generally the case when a thermal conductivity type of detector is used (*2*, *5*, *9*). It then becomes necessary to multiply each component elution area in a mixture by a distinctive factor in order to make the elution areas proportional to component mole concentrations. The calibration procedure used to obtain these factors has been discussed by Keulemans *et al.* (*6*), Dimbat *et al.* (*4*), and Rosie and Grab (*11*).

The "internal standard" method introduced by Ray (*10*) provides still another means for obtaining quantitative calibration data.

The necessity for a calibration procedure for the complete analysis of any mixture would be eliminated if one could (a) evaluate these calibration factors from some property or properties of the component and (b) demonstrate that the factor associated with a given component was independent of component concentration. Until the foregoing can be accomplished, it would seem that the significance of the gas chromatographic elution area obtained from thermal conductivity type detectors will remain unknown.

Using data obtained from thermistor type conductivity detectors it has been found that the partial pressure of a pure compound is a linear function of its elution area up to a pressure of 800 mm (1.0 cc sample volume). More important, it was found that the change in elution area per unit change in pressure was proportional to the component vapor density raised to the two-thirds power. This observation may be expressed as follows:

$$A_i = KP_i(\rho_i)^{2/3} \tag{1}$$

$$P_i = K'A_i(\rho_i)^{-2/3}. \tag{2}$$

The general expression for obtaining component mole concentrations from elution areas then becomes:

$$\text{mole \% } R_1 = \left[\frac{A_1(\rho_1)^{-2/3}100}{A_1(\rho_1)^{-2/3} + \cdots + A_i(\rho_i)^{-2/3}}\right]_T \tag{3}$$

where

$A_1, \cdots A_i$ are the integrated elution areas of components $R_1, \cdots R_i$
$\rho_1, \cdots \rho_i$ are the vapor densities of components $R_1, \cdots R_i$, and
T is the temperature at which the analysis is performed.

It is interesting to note that eq. 3 can be obtained if one assumes (with a constant gas velocity) that the heat transfer coefficient h_i of a component is proportional to its vapor density ρ_i raised to the two-thirds power (*8*) and that the component elution area is proportional to the quantity of heat transferred as the component passes by the sensing element. In connection with eq. 3 it can also be shown that

$$\rho = C\left(\frac{\mu Cp}{k}\right)(M)(\alpha)^{-1} = C(Pr)(M)(\alpha)^{-1} \tag{4}$$

where

ρ = vapor density
μ = absolute viscosity
k = thermal conductivity
C_p = specific heat capacity at constant pressure
M = molecular weight
$\alpha = C_p/C_v$
Pr = Prandtl number
C = constant.

The above assumptions are currently being investigated and the results will be published at a later date.

APPARATUS

The instrument used in this investigation was a Perkin-Elmer Model 154 Vapor Fractometer. The instrument employs a conventional thermistor type conductivity detector. The reference and sensing thermistors are placed in opposite legs of a Wheatstone Bridge with the out-of-balance voltage fed to a 0–10 mv recorder. The instrument conditions used are shown below:

Bridge Current = 15.5 ma
Detector Temperature = 25–26°C, 125–126°C
Column Pressure = 10–20 psig
Carrier Gas Flow = 25–60 cc/min.

Helium was used as the carrier gas in this investigation. Substrate supports were 60–100 mesh Celite 545 or 30–50 mesh C-22 firebrick; the supports were impregnated with 25–30 wt per cent substrate in all cases.

The light hydrocarbon mixtures were resolved at 25°C on a tandem column arrangement of dimethylsulfolane (11 feet) + di-*n*-decyl phthalate (6.5 feet); all other mixtures were resolved at 125°C on a tandem column arrangement of Carbowax 350 (6.5 feet) + Perkin-Elmer "C" packing (3.5 feet).

EXPERIMENTAL

In order to check eq. 3 several mixtures of known composition were analyzed. The results obtained are shown in Tables I–V and represent the average of at least three analyses. The known composition of the mixtures was accurate to ±0.05 wt per cent.

Tables I–III include the light hydrocarbon mixtures; the known and found values in Table II do not agree as closely as in Tables I and III, but this can be attributed largely to the fact that propane, propylene, and isobutane are not completely resolved in the mixture.

Table IV shows a typical analysis of a mixture containing heavier hydrocarbons. The non-aromatic portion of this mixture was composed of cyclohexane, methylcyclohexane, *n*-hexane, and *n*-heptane.

TABLE I

PHILLIPS MIXTURE NO. 35

Component	% Found	% Known
propane	5.3	5.2
i-butane	19.7	19.9
n-butane	43.8	44.0
1-butene	20.0	19.8
2-butene (mix)	4.7	5.1
n-pentane	4.4	4.1
1-pentene	2.1	1.9

TABLE II

PHILLIPS MIXTURE NO. 40

Component	% Found	% Known
ethane	4.0	4.0
propane	16.0	16.0
propene	16.4	17.0
i-butane	18.6	19.0
n-butane	8.5	7.9
i- + 1-butene	23.2	23.1
2-butene (mix)	11.3	11.1
i-pentane	1.0	0.9
1-pentene	0.5	0.5
2-pentene (mix)	0.5	0.5

TABLE III

Phillips Mixture No. 37

Component	% Found	% Known
i-butane	3.0	3.3
n-butane	13.8	14.0
i- + 1-butene	24.2	23.8
trans-2-butene	22.0	22.0
cis-2-butene	19.4	19.0
1,3-butadiene	17.6	17.9

Table V includes the analysis of a predominantly non-hydrocarbon mixture. The results obtained on this and the preceding mixtures would seem to indicate that eq. 3 is quite general.

The results obtained on Phillips Mixture #35 using nitrogen, helium, and hydrogen carrier gases are shown in Table VI. From these results it was concluded that eq. 3 became more exact as the thermal conductivity of the carrier gas increased relative to the thermal conductivity of components in the mixture to be analyzed. It might also be concluded that eq. 3 could be applied to any mixture where the carrier gas thermal conductivity was five times greater or less than that of any component in the mixture to be analyzed.

The C_1 through C_4 hydrocarbon vapor densities used in this investigation were obtained from the 1948 edition of the Natural Gasoline Supply Men's Association (NGSMA) technical manual. The vapor densities of these compounds were also calculated from (a) the Berthelot equation of state, (b) the Beattie-Bridgeman equation of state, and (c) compressibility factors obtained from reduced pressure–temperature charts. The choice of the NGSMA vapor densities resulted from the comparative analysis of C_1–C_4 hydrocarbon mixtures using the vapor densities from all these various sources.

In general, it was very difficult to obtain a high degree of internal con-

TABLE IV

Aromatic Mixture No. 3

Component	% Found	% Known
benzene	64.6	64.8
ethylbenzene	21.1	21.4
diethylbenzene (mix)	12.0	11.9
non-aromatics	2.2	2.0

TABLE V

NON-HYDROCARBON MIXTURE NO. 2

Component	% Found	% Known
methanol	21.9	21.9
acrylonitrile	27.9	27.6
n-butanol	28.5	28.6
styrene	21.7	21.9

TABLE VI

PHILLIPS MIXTURE NO. 35

Component	% Found(F)			% Known (*K*)
	N_2	He	H_2	
propane	3.8	5.6	5.4	5.2
i-butane	19.0	20.1	19.6	19.9
n-butane	43.0	43.5	44.0	44.0
1-butene	21.2	20.1	19.8	19.8
2-butene (mix)	5.6	5.0	5.1	5.1
n-pentane	5.0	3.8	4.1	4.1
1-pentene	2.4	1.8	2.0	1.9
$(K\text{-}F)^2/n$	1.005	0.093	0.020	0

sistency in vapor density data unless one relied on values calculated from equation of state or compressibility data. With the exception of the C_1–C_4 hydrocarbons the vapor densities of all components were calculated from critical data (*7*) and the Berthelot equation of state.

The calculated vapor densities of benzene and methanol at 398°K were 2–3 % too high assuming that eq. 3 was valid. The calculated vapor density of methane at 298°K was also 2–3 % too high, but the experimentally determined vapor density reported in the NGSMA technical manual gave satisfactory results when used in eq. 3.

The elution areas used in this investigation were obtained with a compensating polar planimeter. The general shape of the elution curves was actually intermediate to that of Gaussian and Maxwellian distributions and accounted for the use of integrated elution areas rather than approximate elution areas as described by Cremer and Muller (*3*). In general, it was found that approximate elution areas could not be substituted for integrated elution areas. The major exception to this observation was found in methane-free light hydrocarbon mixtures. In the event of diffuse or poorly resolved elution curves there was little choice but to use integrated elution areas.

It should be emphasized that the data in this communication was obtained from thermistor type conductivity detectors with the sensing element of the detector in the direct path of the gas stream.

The validity of eq. 3 has not been checked with data obtained from heated wire conductivity detectors. Eq. 3 would be expected to apply to both types of detectors if the heat transfer mechanism is the same for both detectors.

Acknowledgment

The authors are indebted to N. Hadden for the experimental data on the aromatic mixtures and to T. D. McMinn, W. F. Hamner, R. F. Wall, and J. F. Draffen for many helpful suggestions concerning the significance of gas chromatographic elution areas.

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CHAPTER IV

The Behavior of the Solid Support in Gas-Liquid Partition Chromatography

THERON JOHNS

Beckman Instruments, Inc., Fullerton, California

The general requirements for the solid support used in gas-liquid partition chromatography are: (1) the material must have a high surface area: (2) it must not break up under reasonable compaction or under the handling procedure required to prepare the material and fill the chromatographic column; (3) the material must pack uniformly in the column; (4) it must be chemically inert towards the samples which are to be put through the column; and (5) the material must not be appreciably adsorptive.

Experience has shown that various types of diatomaceous earth best fulfill these requirements. James and Martin (*1*) used acid washed Celite 545 in their first experiments in gas-liquid partition chromatography. This material is a diatomaceous earth with an average particle size of 20–40 microns. Subsequent investigations by Dimbat *et al.* (*2*), by Keulemans and Kwantes (*3*), and by the author have established that coarser grades of diatomaceous earth of the types used in Johns-Manville C-22 firebrick and Sterchamol No. 22 firebrick are generally superior to Celite 545.

This paper is an extension of the work on the solid support previously conducted by the author and reported in Beckman Application Manual No. 80875 on Gas Chromatography. The original work showed that columns prepared from Johns-Manville C-22 firebrick gave the best resolution between saturated and unsaturated hydrocarbons. This investigation has now been extended to other classes of sample components with particular interest being paid to the influence of the solid support on the peak shape of the different classes of compounds.

All of the work reported in the present paper was conducted with 6 ft stainless steel columns with an outside diameter of $\frac{1}{4}$ in. A temperature of 130°C was used in all cases. The two partition liquids employed, Silicone 550 and Carbowax 600 (polyethylene glycol with a molecular weight of approximately 600) were coated on the solid support at a ratio of 31.5 per cent by weight. Close grading of the solid support was accomplished by wet screening followed by oven drying.

The first phase of the present work was directed towards determining the influence of particle size of the solid support on the retention times of the eluted sample components, on pressure drop of the column, and on the

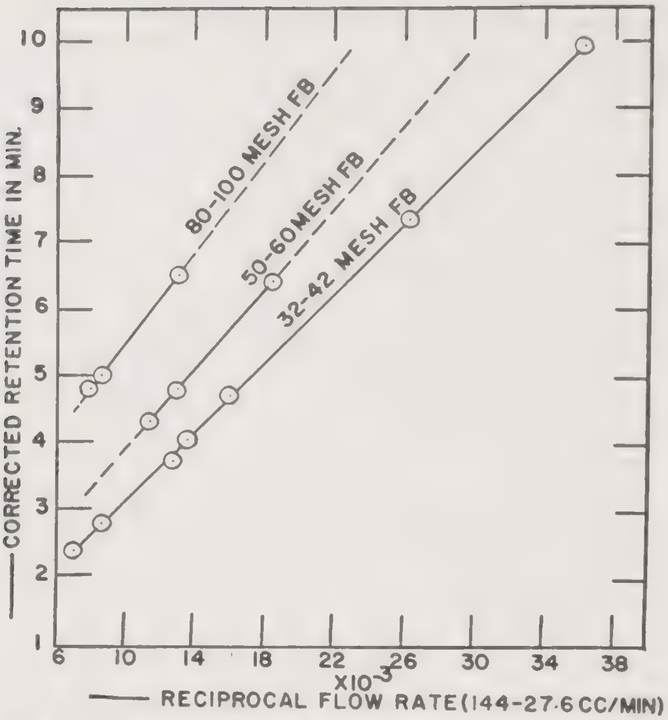

FIG. 1. Effects of particle size and flow on the corrected retention time of butyl acetate.

resolution between components which were deliberately chosen so that only partial separation was obtained on a Carbowax 600 column.

Figure 1 shows the effects of particle size of the solid support and flow rate of the carrier gas on the corrected retention time for butyl acetate through Carbowax 600 columns. The measured retention time was corrected for the dead volume of the columns by subtracting the retention time for air under the same conditions. It is noteworthy that the corrected retention time is inversely proportional to the flow rate or directly proportional to the reciprocal of the flow rate. This relationship held for the different particle sizes but the proportionality constant changed.

This effect is demonstrated more clearly in Fig. 2 where the flow rate was held constant. The results shown indicate that the corrected retention time of a component is inversely proportional to the particle size of the solid support, i.e., as the particle size is decreased the retention time of a component increases even if the flow rate of carrier gas through the column is held constant.

In addition to its effect on the retention times of the sample components, the particle size of the solid support also has a marked effect on the pressure drop of the column and on resolution. Figure 3 shows that the pressure drop of the column is inversely proportional to the particle size at constant

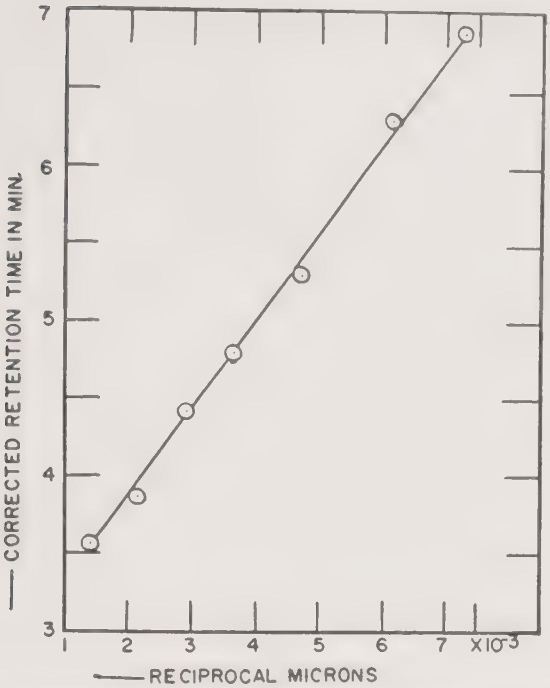

FIG. 2. Effect of particle size on the corrected retention time of butyl acetate at a constant flow rate.

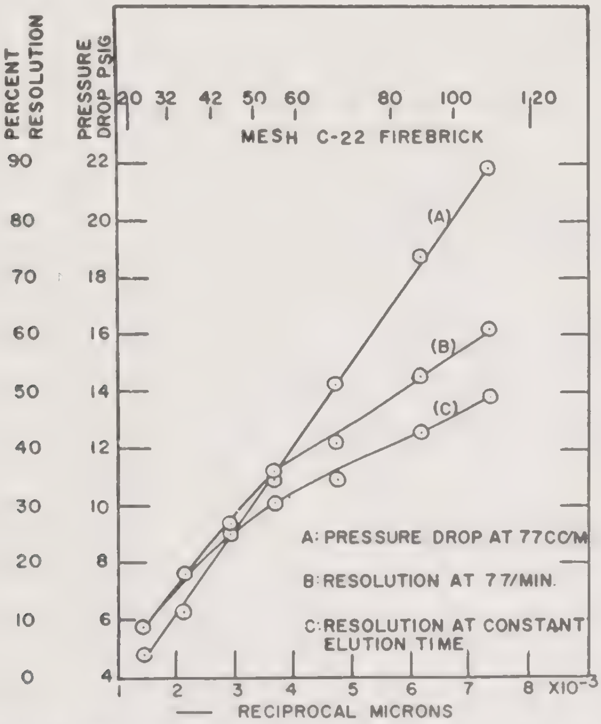

FIG. 3. Effect of particle size on column pressure drop and resolution.

flow rate. At a flow rate of 77 cc/min the pressure drop of C-22 firebrick varies from less than 1 lb/ft to more than 3 lb/ft as the particle size is decreased from 840 microns (20 mesh) to 125 microns (120 mesh). Resolution as shown was measured by the ratio of the depth of the valley between ethanol and methyl ethyl ketone to the height of the methyl ethyl ketone peak. This ratio was then multiplied by 100 to obtain per cent resolution. Figure 3 shows that resolution does increase as particle size is decreased but the rate of increase drops off as particle size decreases. When efficiency of resolution and pressure drop of the column are both considered, these results indicate that a particle size of about 30 to 70 mesh gives the most efficient compromise. Further, if columns with reasonably reproducible elution times and resolution are to be made, the particle size must be controlled as closely as possible, since these factors vary widely even over the range of 30 to 70 mesh.

The second phase of this investigation was concerned with a comparison of several types of diatomaceous earth with respect to the peak shape obtained with components representing several classes of organic compounds. As shown in Figure 4, 5, and 6, the types of diatomaceous earth compared were Chromosorb, C-22 firebrick, Dicalite, Lompoc celite, and Celite 410. These materials were all compared under the same conditions of column length, temperature, type of sample, and type of partition liquid. The partition liquid, Silicone 550, and the sample components were selected so that if the solid support had any adsorptivity some tailing of the peaks would be evident. The asymmetry of the peaks was further magnified by using a fast chart speed of 1⅛ in./min. Of all the materials tested, Chromosorb

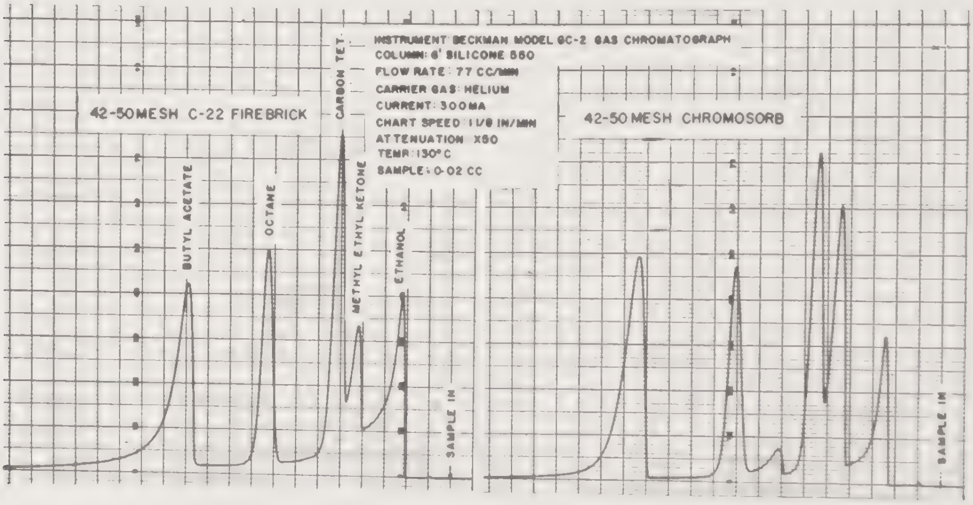

FIG. 4. Resolution and peak shape on C-22 firebrick and Chromosorb. Column: 6′ silicone 550; Flow Rate: 77 cc/min; Carrier Gas: helium; Current: 300 ma; Chart Speed: 1⅛ in/min; Attenuation: ×50; Temp.: 130°C; Sample: 0.02 cc.

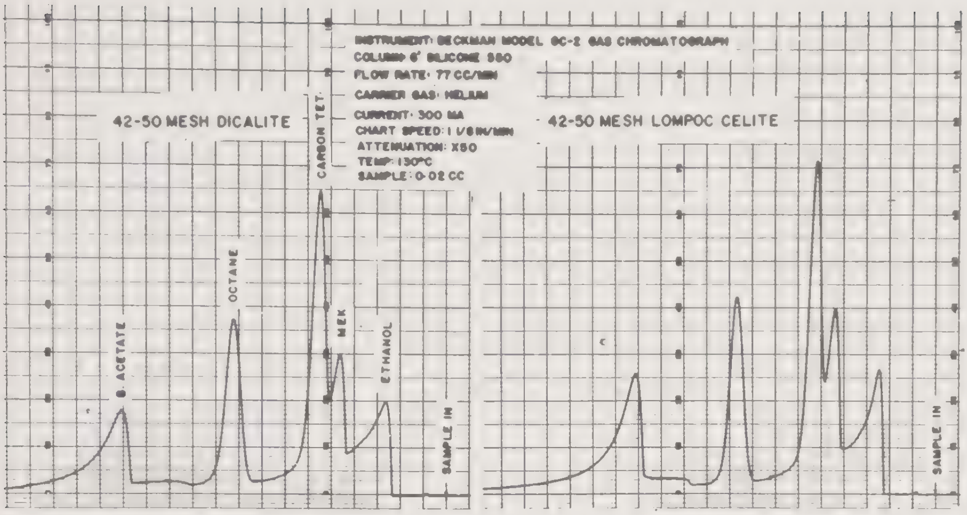

Fig. 5. Resolution and peak shape on Lompoc celite and Dicalite. Column: 6′ silicone 550; Flow Rate: 77 cc/min; Carrier Gas: helium; Current: 300 ma; Chart Speed: 1⅛ in/min; Attenuation: ×50; Temp.: 130°C; Sample: 0.02 cc.

and C-22 firebrick showed the least adsorptivity, with Chromosorb being slightly better than C-22 firebrick in this regard. Severe tailing of the peaks near the base line was found to be associated with the adsorptivity of the solid support and not due to any solution effect of the partition liquid.

Peak tailing of the magnitude shown with ethanol and butyl acetate makes it virtually impossible to obtain reproducible results with repeated sampling. It also results in an inaccurate signal from a single sample since

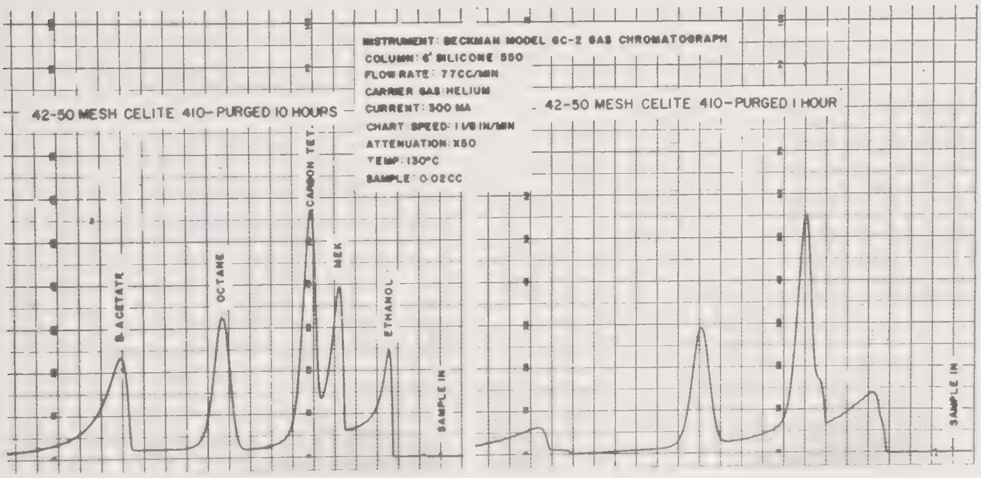

Fig. 6. Resolution and peak shape on Celite 410. Column: 6′ silicone 550; Flow Rate: 77 cc/min; Carrier Gas: helium; Current: 300 ma; Chart Speed: 1⅛ in/min; Attenuation: ×50; Temp.: 130°C; Sample: 0.02 cc.

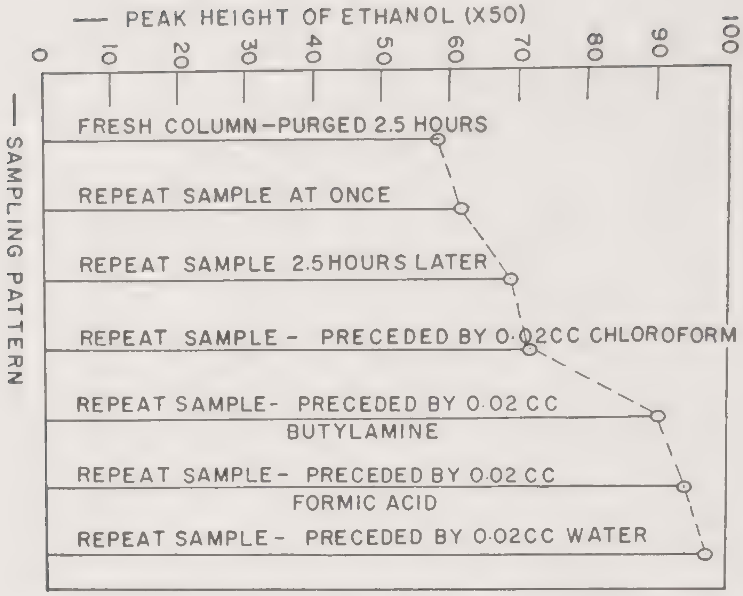

FIG. 7. Column improvement caused by repeat sampling.

a portion of the component is more or less permanently adsorbed on the surface of the solid support.

Figure 6 indicates that the adsorptivity of the column material can be diminished by continued purging of the column with the carrier gas and/or repeated sampling with the sample being tested. This effect was tested further as shown in Fig. 7. In this case the improvement of the column was measured by the increase in the peak height of ethanol since diminishing of the tail of the peak was reflected in increased peak height. Purging of the column was found to give only a very slight improvement of the column. Repeated injection of samples which show tailing will give a significant improvement in the column at least in so far as that particular sample is concerned. The sharp improvement shown by injecting a sample of butylamine in the column indicates that if a strongly adsorbed material is contacted with the solid support, then any component which is less strongly adsorbed will pass through the column without appreciable tailing. It also shows that while the tendency of C-22 firebrick to adsorb polar components is strong, the capacity is very low since a sample of only 0.02 cc of butylamine was sufficient to remove most of the adsorptivity towards ethanol. Figure 8 shows the chromatograms corresponding to the first and last samples in this series. Note the change in the peak shapes of ethanol and butyl acetate and the improvement in resolution between methyl ethyl ketone and carbon tetrachloride.

It was first thought that this improvement in the column towards the test sample might be due to a change in pH caused by the injection of

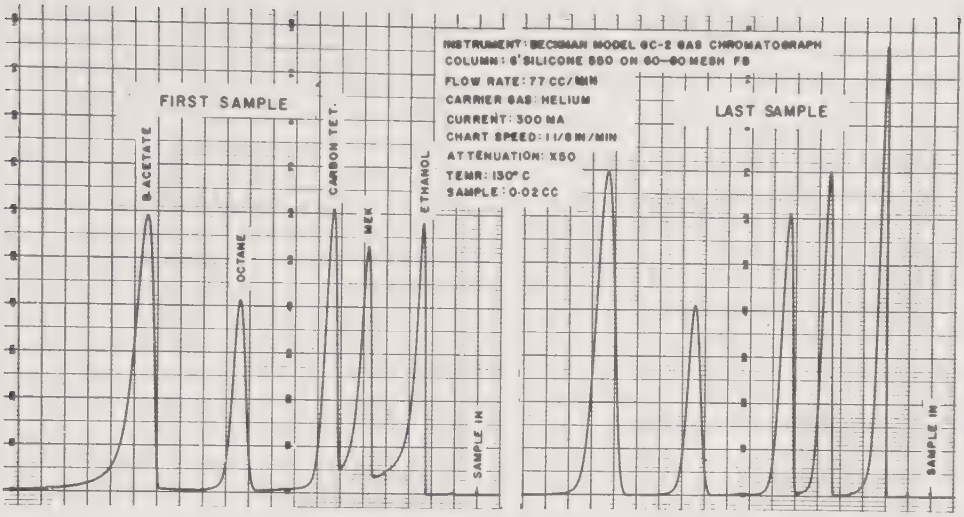

FIG. 8. Variation of column due to sampling. Column: 6′ silicone 550 on 60-80 mesh FB; Flow Rate: 77 cc/min; Carrier Gas: helium; Current: 300 ma; Chart Speed: 1⅛ in/min; Attenuation: ×50 Temp.: 130°C; Sample: 0.02 cc.

butylamine or that the adsorptivity of the firebrick was due to acid soluble materials. However, samples of firebrick which were acid washed with dilute HCl, adjusted to a pH of 7–8 with NaOH or NH_4OH, and then oven dried did not show any significant improvement when the test sample was run. It was concluded from these results that pH is not generally the controlling factor in the adsorptivity of the solid support.

This conclusion was tested further as shown in Fig. 9 by comparing the

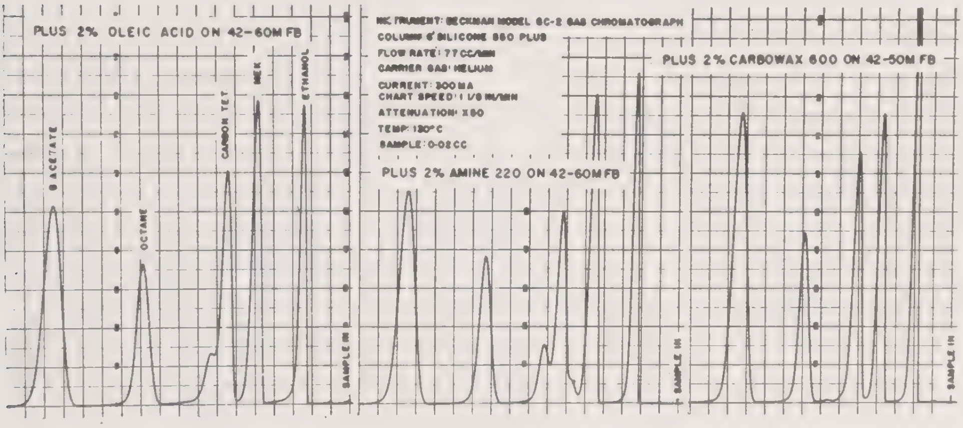

FIG. 9. Effect of adding trace amounts of highly polar compounds to Silicone 550. Column: 6′ silicone 550 plus; Flow Rate: 77 cc/min; Carrier Gas: helium; Current: 300 ma; Chart Speed: 1⅛ in/min; Attenuation: ×50; Temp.: 130°C Sample: 0.02 cc; Plus 2% amine 220 on 42–60 MFB.

effect of adding very small amounts of an acid (oleic acid), a base (Amine 220), and a relatively neutral material (Carbowax 600) to the Silicone 550 partition liquid. At a concentration of two per cent by weight these compounds did not affect the order of elution of the components of the test sample. However, each of the compounds was very effective in reducing the tailing of the ethanol and butyl acetate peaks. This indicates that adsorptivity of compounds on C-22 firebrick is related to the polarity of the compound and, if a high polarity material is deliberately contacted with the solid support, any component with a lower polarity will not be adsorbed to an appreciable degree. The pH of the material can be important if acidic or basic sample components are to be run. In this regard one should not deactivate the solid support with a basic material if acidic samples are to be analyzed.

Water and the lower fatty acids still exhibit tailing under the conditions shown in Fig. 9. It should be possible to improve this situation by using a solid support with less surface area, less adsorptivity, and/or by adding a greater quantity of a very strongly adsorbed compound to the partition liquid.

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DISCUSSION

ANONYMOUS: I would like to ask what the total concentration of the partitioning liquid was.

JOHNS: The total concentration of the Silicone 550 was 30 per cent by weight. The concentration of the very polar material which I was using to deactivate the column to cut down the adsorptivity was 2 per cent. This was not sufficient to change the order of elution of the various components. Now, if I had used a partitioning liquid with the material that I used for deactivating the brick, I would have changed the order of elution of the various components.

ANONYMOUS: You have made a study, then, of the various concentrations of the partitioning liquid?

JOHNS: I have looked at a few other concentrations, both lower and higher, and adding more material did not seem to cut down the tailing which I objected to. Incidentally, I have exaggerated the appearance of these slides by using a very fast recording chart speed. You could make the chromatograms look better; however, the influence that they have on the accuracy of your analysis is fixed, so just making them look better does not really improve your quantitative accuracy.

KIRKLAND (*E. I. du Pont de Nemours & Co., Inc., Delaware*): If I am not mistaken, Dr. Martin proposed a very interesting way of overcoming this: if you take Celite 545 and treat it with alcoholic or aqueous sodium hydroxide you can deactivate the silicate surface this way and, thus, cut down the tailing effects. Actually, there are acidic Si-OH groups on the surface of the untreated Celite. By reacting these acidic groups with sodium ion, a large portion of the surface is deactivated, thus reducing the tailing phenomena. We routinely deactivate Celite 545 and in this manner eliminate a lot of the tailing problems not only with amines, but with alcohols, ketones, and other highly polar compounds.

JOHNS: I think, in this case, that the partitioning liquid with which you coat the solid support after you have treated it would also have a tremendous bearing on the results. I indicated that when you are running acidic or basic components the pH condition in which you have left your fire brick will make a difference. I believe the work that Dr. Martin did in running fatty acids illustrates this. He first treated his material with dilute acid to remove iron. The partitioning material that he used was stearic acid added to some other material. I believe that probably the stearic acid contributed to a large degree to the good results that he obtained.

KIRKLAND: I would like to point out the difference of the two techniques that we are discussing. In your case you are covering up the active sites chemically by adsorption. In the process that I was discussing, however, we were actually chemically reacting the active sites with a material which will then be essentially permanent.

HOLMGREN (*Hoffmann-LaRoche, Inc., New Jersey*): A by-product of treating these supports with alkali that we have found (and that probably everybody else in the room has found) is that catalytic centers on the support are destroyed, or at least their effect is minimized. We have had a series of tertiary and alpha-beta unsaturated primary alcohols dehydrate on untreated siliceous supports. Merely by soaking the support in 10 per cent sodium carbonate before impregnation, that effect of dehydration has been minimized strongly, and in some cases entirely eliminated. I might also say this dehydration is apparently caused by the silica, because it happens also on sand. It is strongly affected also by the nature of the stationary liquid phase. For example, with an unsaturated 5-carbon tertiary alcohol, we have obtained a great deal of dehydration with an ester substrate and very little with a Carbowax substrate on the same fire brick.

CHAPTER V

The Interrelationship of Column Efficiency and Resolving Power in Gas Chromatography

STEPHEN S. OBER

Abbott Laboratories, North Chicago, Illinois

Much has been written and said concerning gas chromatographic column efficiency. One of the most familiar and comprehensive studies of the subject is that reported by Keulemans, Klinkenberg, van Deemter, and others (*1–3*). Their work is of tremendous value. By their own word, however, there is still much to be done to fill the large gap between theory and the everyday practice of selecting a stationary phase for a given separation. In this paper an experimental method for evaluating stationary phases is proposed. This method makes use of a modified version of van Deemter's theoretical plate equation. This modification is such that column efficiency and resolving power together are determined, and information is obtained pertaining to the stationary phase which will separate best a given set of solute components.

DEFINITION OF TERMS

Column Efficiency and Solvent Efficiency Factor

Column efficiency has been measured by the height equivalent to a theoretical plate. The theoretical plate has been defined as the column space necessary for attainment of solute distribution equilibrium between the moving gas and the stationary liquid phases. This column property is related to such parameters as elution gas flow rate, column temperature, solute, and solvent physical properties. Yet efficiency is a poor word to use here. The HETP value of a column is really a measure of the column's deviation from ideal, linear chromatography. This is particularly true when the ascribed method of evaluation of HETP is used, *viz.*, $(l/16)\ (x^2/y^2)$, where l is the length of the column, x is the extrapolated triangle base, and y, the retention time of the solute in question (*4*). Nothing in this expression refers to the column resolving power.

It can be seen that the above described HETP value reflects over-all column efficiency. It is the objective in this proposed experimental technique to rate the stationary solvent phases quantitatively on a basis of solvent contribution only. This is not easy, but it is here that the van Deemter equation offers a possible solution to the problem.

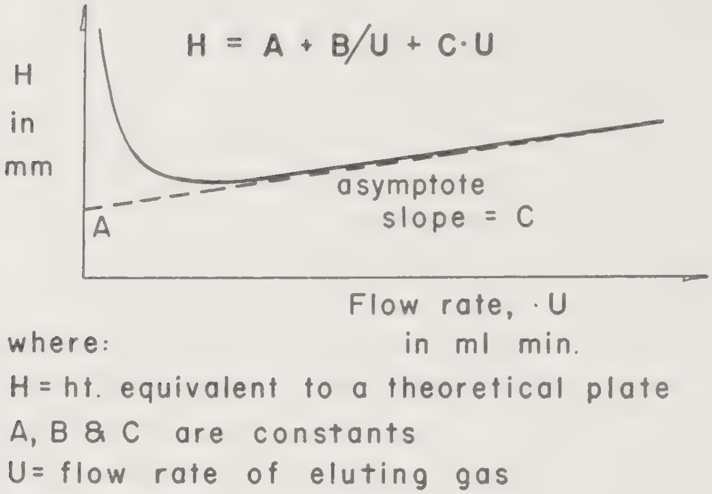

FIG. 1. Van Deemter equation for the height equivalent to a theoretical plate.

The van Deemter equation (Fig. 1), which relates most of the parameters of gas chromatography (for a single component) to the HETP value, shows how at least part of the packing characteristics and other non-solvent properties of the column and detector can be divorced from those of the solvent alone. Thus, the constant *A* is dependent upon how the column is packed and upon the inert support for the stationary phase. The constant *B* is a factor dependent upon both the column packing and the diffusion of the solute in the moving gas phase. And the constant *C* is dependent upon the nature of the liquid stationary phase (the solvent) as well as upon the physical state of the phase in the column. This latter dependency is most unfortunate, but as will be seen, *C* has been used despite this drawback in the rating of the contribution of the solute–solvent relationship to the HETP value of the column. Thus, *C* has been termed the solvent efficiency factor. Notice that for large values of the gas flow rate, *U*, *C* is given by the slope of the asymptote, or *C* can be calculated from any three points on the HETP vs *U* curve. Further explanation of this equation can be found in Keuleman's book on gas chromatography (*1*).

Resolving Power and Resolving Power Characteristic

Resolving power can and does have many names—resolution, separation, separation factor. There are an almost equal number of definitions of this property. One accepted definition is that of separation factor, proposed by Glueckauf (*5*). Glueckauf used the concept of error function complements for overlapping Gaussian distributions to derive an expression relating the degree of separation and the number of theoretical plates required for that degree of separation. In order to use the calculation, or the handy chart drawn up from the derived equation, for the purpose of selecting a solvent suitable for a given separation, the following data must be known or determined:

(1) Latent heat of vaporization of each solute component.

(2) Heat of solution for each solute component in the stationary liquid phase.

(3) Partial pressure of each solute component at the temperature of operation of the column.

(4) Partition coefficient between the moving gas and the stationary liquid phase for each solute component.

These data for most systems of interest are difficult to determine. Thus, in practice the tendency is to avoid Glueckauf's equation and to resort to trial and error. If the list of separations is long and varied, the trial and error method goes on and on and on, always with no guarantee of success. Furthermore, it is doubly unfortunate that any given trial probably is of little value for any other separation.

The present paper is aimed at establishing an experimental practice capable of yielding the maximum possible information about not only the separation under study but also information about similar solutes and their separations. With this purpose in mind the resolving power of a solvent with respect to a given solute pair is defined as the time interval between the peak maxima of each solute divided by the average elution time.* This is shown in Fig. 2. Here the difference in retention times (the time interval) between peak maxima is equal to $Y_2 - Y_1$.

In order to combine the two solvent effects, which constitute the solvent's contribution to the overall performance of the column, the average of the two C values for the two components being separated is divided by the resolving power (in order to keep the resultant quantity an inverse function comparable to the HETP concept). This quantity is called the resolving power characteristic. It is indicative of both the resolving power and the column efficiency with respect to the solute pair–solvent system tested.

The distinction between column efficiency and resolving power can be visualized best by looking at extreme examples of each property. In Fig. 3, three columns alike in every respect except for the nature of the liquid

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* The retention volumes considered in the differential quantity designated resolving power should be corrected for the dead volume of the column. This is done so that the values, if desired, can be directly related to the ratio of component retention volumes (the usual separation factor) and the corresponding thermodynamic properties of the systems being tested. The non-identity of the expression for limiting values as the components' retention times approach that of air is not considered to be a serious fault of the system in as much as nothing close to this limiting condition will be approached in practical experimentation.

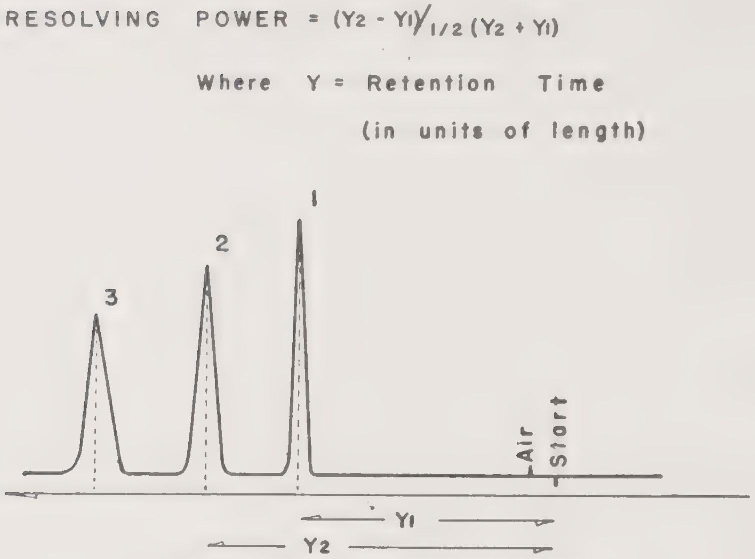

Fig. 2. Definition of resolving power.

stationary phase have been used with a solution consisting of three components. In Case 1 the component maxima are well separated, but the column is very inefficient as judged by the HETP test. In Case 2 another stationary phase has very high column efficiency according to its low HETP value, but it has failed completely to resolve the three components. In Case 3 high column efficiency and resolving power are combined to the point of complete component separation, although the maxima are no farther apart than in Case 1. Clearly, both column properties, resolution and efficiency, are required to define fully the quality of gas chromatographic data.

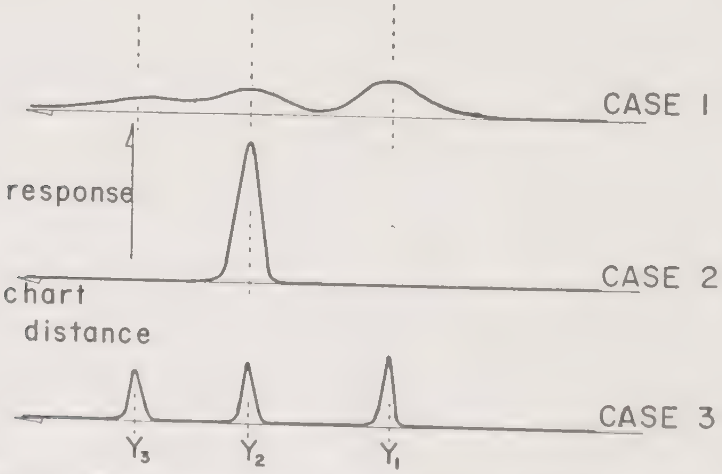

Fig. 3. Possible chromatograms of a 3-component mixture.

EXPERIMENTAL

Selection of a Test Solution

Since the proposed technique is designed to evaluate the ability of solvents to separate structural isomers, the first step is to select a suitable test solution. In the present study esters are taken as the class of organic compounds to be separated. The problem of which esters should make up the test solution involves consideration of several factors.

a. Since initial members of a homologous series, such as methyl acetate, are not representative of the higher members of the series with respect to the controlling physical-chemical properties, a mixture of esters containing at least five carbon atoms is indicated. Esters of ten or more carbon atoms, on the other hand, would necessitate higher operating temperatures and would make more difficult separations of the various isomer pairs.

b. A test solution is desired which will be as representative of as many of the types of separation problems anticipated in future work as possible.

c. The test solution should include as many of the isomers as are readily available even though only a few of the members are of current interest, since the additional data will then be available for subsequent evaluation without the need for additional experimentation.

The ester test mixture which in general best fulfills these requirements, without at the same time being overly complicated, contains normal pentyl, iso-pentyl, neo-pentyl, 2-pentyl, 3-pentyl, and 2-methyl-2-butyl acetates in unequal weight proportions. Such a $C_7H_{14}O_2$ ester mixture will serve to test solvents for the separation of all saturated, non-aromatic, and unsubstituted esters of the six basic types represented. Although the six isomers of $C_7H_{14}O_2$ selected are not completely representative of the nearly forty others which exist, strict correlation may not be necessary in many cases. Thus, as a general rule, when the separation of primary isomers is of interest, the separations of normal pentyl, isopentyl, and neopentyl are indicative. Similarly the resolution of secondary ester structures can be predicted from the behavior of 2-pentyl and 3-pentyl acetate. (The separation of a C_8 from a C_7 ester is considered so easy that a refined technique such as the one being proposed here is not necessary.)

Experimental Technique

With a suitable test solution available, it might seem that a series of chromatograms could now be run at varying flow rates for each stationary liquid phase of interest to provide all of the data needed. Unfortunately, the task is not that simple. Just any chromatographic run cannot be used to calculate a quantitative value of HETP (and the corresponding *C* constant from a series of three or more HETP values at varying flow rates). Both the peak base dimension and the retention volume are dependent upon the sample size, and this dependence must be taken into account by extrapolation to zero sample size.

Illustrative plots of both the extrapolated peak base width and the retention time (at constant flow rate) as a function of sample size are shown in Fig. 4. If the gas chromatographic unit has constant and reproducible flow rate control, only four to five points are needed to allow extrapolation. While very small samples theoretically can yield nearly accurate data concerning these limiting values, the small sample itself introduces a larger measuring error. Consequently, it is advisable to extrapolate from a series of reasonable sample sizes, all run at high sensitivity. In the examples chosen for Fig. 4, the largest sample volume used was less than 0.01 ml.

For each solvent to be tested extrapolation to zero sample size gives an X_0 and a Y_0. These data are gathered for at least three flow rates. The limiting values of the retention time (Y_0) and the peak base width (X_0) are then used to calculate HETP values for each component for each flow rate according to the standard column efficiency formula. (Note: It is generally advisable for these calculations to select the same three flow rates close to and beyond that flow which provides a minimum HETP.) Flow rates are measured (and, if necessary, corrected for flow at the column temperature), and HETP–flow rate curves drawn. From these curves average van Deemter constants can be obtained.

Resolving power values are also calculated from Y_0 data for each combination of solute pairs. As explained in the previous note the Y_0 values should be corrected for column pressure drop and for the dead volume of the column, if the values are also to be used to evaluate the thermodynamic properties of the solute–solvent system.

As a final step, wherever the constancy of the van Deemter A values warrants, the average of the two solute component C constants is divided by the resolving power to obtain the value of resolving power characteristic which rates the solvent on the basis of efficiency and resolution (over-all performance) for the solute pair tested.

Illustrative Data

Selected data from our solvent testing program with esters will be given by way of illustration. These data are restricted to solvents which ordinarily are rated as excellent for resolving esters. In order to simplify the illustration only three of the primary pentyl acetates in the suggested ester test solution will be considered.

In Fig. 5 a typical chromatogram of the three pentyl acetates selected is shown. The conditions used for this chromatogram and throughout that

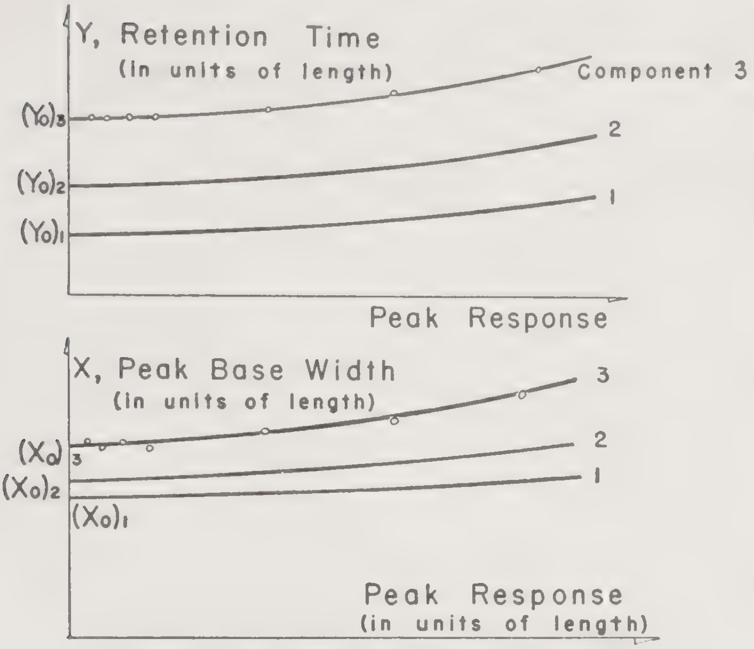

FIG. 4. Determination of X_0 and Y_0.

part of our testing program from which illustrative data will be drawn were: temperature, 100°C; eluting gas, helium; 6′ x ¼″ copper tubing (wound); ground firebrick of 25 to 60 mesh, coated with 25% (w/w) of solvent; gas cross-sectional column area, 13.6 mm^2; temperature of liquid sample introduction system, 150°C; and detector, thermal conductivity of the filament type. The three solvents for which data will be presented are Apiezon N, Linde silicone oil, L-46, and a mixed solvent whose composition will be given.

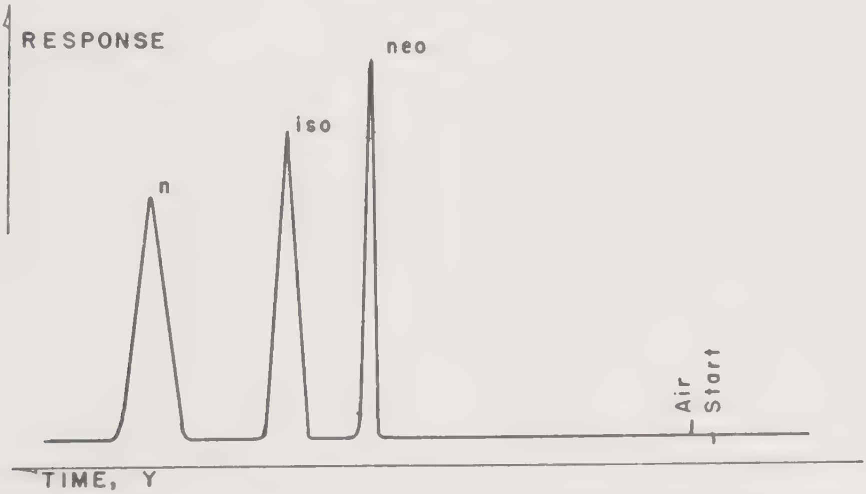

FIG. 5. Chromatogram of neo-pentyl, iso-pentyl, and *n*-pentyl acetate.

TABLE I

Typical Column and Solvent Efficiency Data

	HETP (mm)	A (mm)	C (sec)
Normal pentyl acetate:			
Apiezon "N"	1.70	1.5	0.024
Silicone oil (Linde-46)	1.73	1.7	0.023
Mixture[a]	1.54	1.6	0.020
Isopentyl acetate:			
Apiezon "N"	1.71	1.6	0.024
Silicone oil (Linde-46)	1.74	1.6	0.023
Mixture[a]	1.56	1.6	0.020
Neopentyl acetate:			
Apiezon "N"	1.61	1.4	0.020
Silicone oil (Linde-46)	1.63	1.4	0.020
Mixture[a]	1.48	1.5	0.014

[a] A mixture of benzoic acid (2%), diethylsebacate (2%), polyethylene glycol 6000 (48%), and polyethylene glycolmonostearate 6000 (48%).

Illustrative data obtained with the three solvents noted appear in Tables I and II. Table I lists the HETP values and the van Deemter constants, *A* and *C*. The values for *C* were calculated from the HETP–flow rate data. *A* values, wherever they are constant for different solvents, reflect successful efforts to pack each column in identical fashion. The *C* values show

TABLE II

Typical Resolution Data

Pentyl Acetate Pair	Average C (sec)	Resolving Power	Resolving Power Characteristic (sec)
Normal-Iso			
Apiezon "N"	0.024	0.23	0.104
Silicone oil (Linde-46)	0.023	0.30	0.078
Mixture[a]	0.020	0.41	0.048
Iso-Neo			
Apiezon "N"	0.022	0.24	0.092
Silicone oil (Linde-46)	0.022	0.28	0.079
Mixture[a]	0.017	0.22	0.077
Normal-Neo			
Apiezon "N"	0.022	0.47	0.047
Silicone oil (Linde-46)	0.022	0.58	0.038
Mixture[a]	0.017	0.63	0.027

[a] A mixture of benzoic acid (2%), diethylsebacate (2%), polyethylene glycol 6000 (48%), and polyethylene glycolmonostearate 6000 (48%).

some divergency, as anticipated, if they truly reflect the varying nature of the solvents.

Neither the HETP figures nor the C values bring out clearly the significant difference between the three liquid stationary phases. Here is where resolving power and resolving power characteristic enter the picture. These data are given in Table II and serve to distinguish the solvents quite adequately. Notice that resolving power is greater the larger the number, similar to when column efficiency is reported as the number of theoretical plates per unit of column length. Resolving power characteristic, however, is an inverse function analogous to the concept of HETP.

CONCLUSIONS

The rating of solvents by means of both their efficiency (in the sense of contribution to the deviation from ideal-linear chromatography) and their resolving power accomplishes many objectives.

1. Random testing of solvents is eliminated. This means eventual laboratory time is saved in attempting difficult separations. Extremes in whatever solvent properties are deemed to be of value are tested first and from their efforts on the solute pair of interest classes of solvents can be shown to be of no value—or worth investigating further. For example, combination solvents appear to be preferable and worth additional detailed study.

2. A check on packing uniformity and over-all column efficiency is obtained. In these days of ever increasing column efficiency, the significance of separation performance data is questionable unless this factor is taken into account.

3. The subtle differences between chemically similar solutes and of the relationship of these differences with respect to selected solvents are magnified. Indeed this was the very reason for creating resolving power and resolving power characteristic. In Table II note the values of resolving power characteristic for the combination solvent for the first two components. The mixed phase is obvicusly preferred for this particular separation.

4. An intelligent prediction of the separation ability of a particular solvent for certain solutes not tested directly can be made. Thus, if a separation of two primary ester isomers of boiling points in excess of 300°C is desired, the separation behavior of the primary C_7 esters is followed (at *ca.* 100°C) for every solvent deemed to be worth investigating. From the rating data so gathered the field is narrowed down, if not to one, at least to two or three solvents which then can be tested directly.

In the future it is hoped that data gathered from this experimental rating technique will permit adequate prediction of solvent resolving power for a particular separation from a knowledge of the physical properties of the solutes and solvent. Perhaps also it will be possible to estimate the ultimate separation attainable. Like the ultimate in practical column efficiency, the best attainable separation of any solute pair is a complete unknown at the present time.

Acknowledgment

Grateful acknowledgment is made to Nancy D. Sanderson and Joan M. Zimmer for their help in obtaining the data for this paper. Thanks are also due Dr. K. J. Frederick of Abbott Laboratories and Mr. Seaton Preston of Podbielniak Inc., for their help in the conduct of this study and in the preparation of the manuscript.

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Discussion

JONES (*E. I. du Pont de Nemours & Co., Inc., Delaware*): Regarding the van Decmpter equation, we believe it is a very good equation; however, we also believe that it represents an oversimplification of certain points, namely the high velocity term (the coefficient C that was referred to).

OBER: Yes, we, too, feel that the coefficient C is an oversimplification, and the paper presented attempted to make allowances for this suspicion.

CHAPTER VI

Gas Chromatography Instrumentation for the Laboratory

C. PHILLIPS

Merton College, Oxford, England

INTRODUCTION

Gas chromatography consists of a process in which at one end of a column you push in very rapidly a whole collection of substances and then at the other end you sit back and watch each substance emerge in its own characteristic time. Most of the instrumentation of gas chromatography has been connected with the ingenious vapor detectors which have been constructed for watching the substances emerge, and to a lesser extent with devices for the virtually instantaneous introduction of small samples. I propose to say very little about these, and to concentrate rather on the processes which are taking place inside the column. By so doing I hope to illustrate some of the many ways in which gas chromatography can be used for the solution of laboratory problems.

The emergence of each substance is normally recorded as a peak in a chromatogram. Each peak possesses two important characteristics (*9*)

(1) The retention time of the peak maximum.

(2) The spread of the peak. This is generally measured in terms of the number of theoretical plates, to which the column is approximating in its behavior, a good and soundly operated column being equivalent to a large number of plates.

Separation of two substances is assisted by a large retention time ratio, or separation factor, and by using a column with many plates. The relations between the two characteristics have been formulated most clearly in a diagram due to Glueckauf (*2*) which is reproduced in Fig. 1. From this diagram one may deduce the degree of separation (i.e., η the fractional impurity left in each substance if a cut is made at such a point that the fractional impurity will be the same for both substances) in terms of the separation factor α, the number of theoretical plates n, and the mol fractions m_1 and m_2 of the substances to be separated. For simplicity we may restrict our attention to the case of a 1:1 molar ratio (for which incidentally the impurity is at a maximum) i.e., $\eta_{1:1}$. Then it will be seen from the figure that the two substances will be separated to 99% purity ($\eta = 10^{-2}$) on a column equivalent to 1000 plates if the separation factor is 1.16, or on

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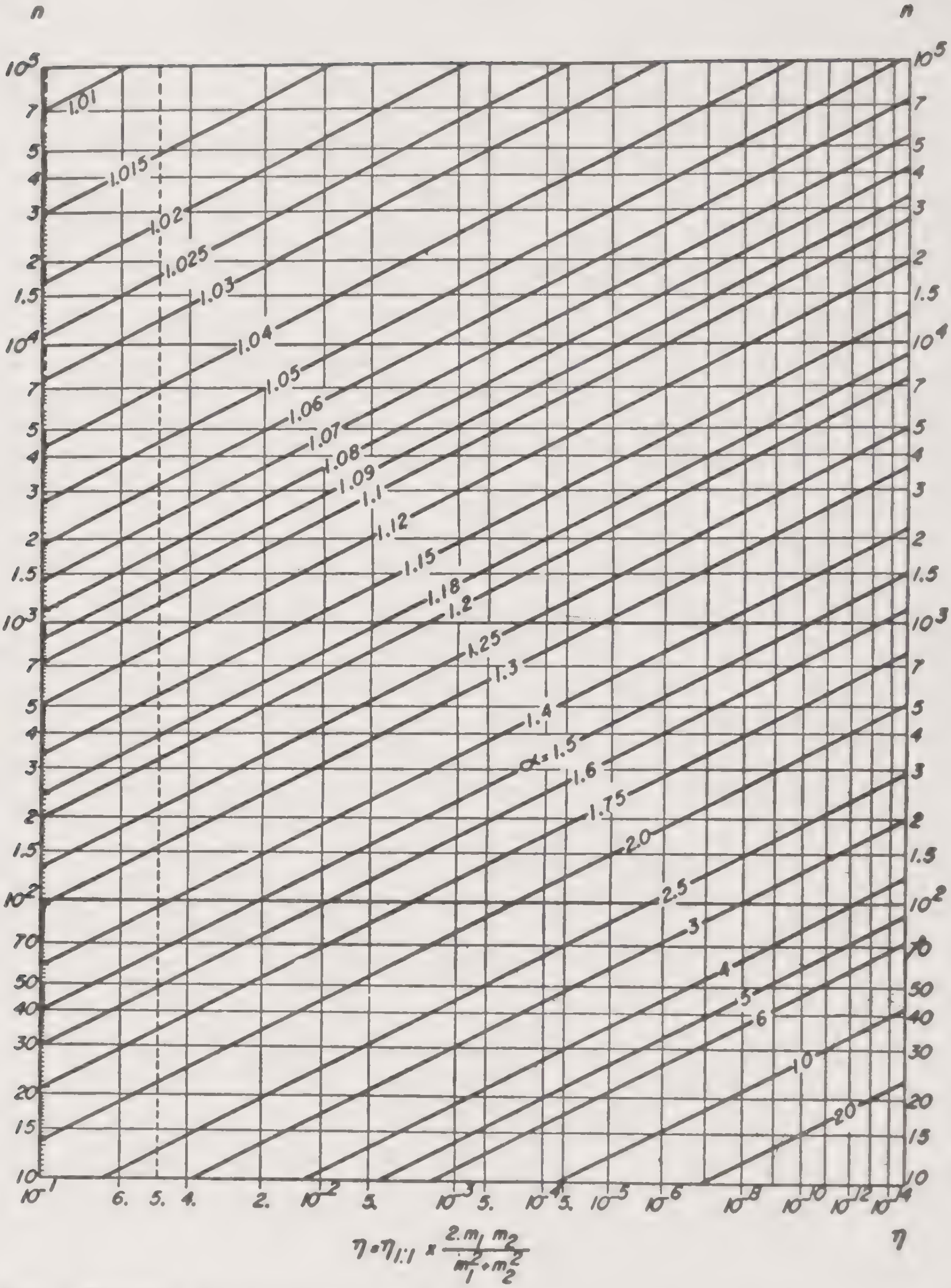

FIG. 1. Relation between number of plates (n), separation factor (α), and fractional band impurity (η). (After E. Glueckauf, courtesy Reinhold Publishing Corp.)

a column equivalent to 10,000 plates if the separation factor is 1.05. Much poorer separations than this will still appear as two peaks, and even worse cases can usually be unravelled into two peaks by noting the abnormally low theoretical plate number of the composite peak.

Theoretical Plates

The consideration of theoretical plate efficiency is a sort of chemical engineering. It has been well summarized by Keulemans (*6*). Reduction of efficiency and consequent increase in the HETP results in the main from four factors.

(*a*) Non-instantaneous introduction of sample. This is reduced by using a small sample size, and hence creates problems of sampling and detector sensitivity.

(*b*) Irregularities and chanelling of flow in the column. These can generally be reduced by efficient packing techniques.

(*c*) Longitudinal diffusion in the gas stream. This can be reduced by using a carrier gas of low diffusivity (e.g., nitrogen instead of hydrogen), a carrier gas at high pressure, and by an increase in flow rate until an optimum is set by the operation of the fourth factor.

(*d*) Slow diffusion into and out of the liquid phase. This effect is less marked with substances of large retention time (high solubility in the liquid phase), so that theoretical plate values tend to rise along any chromatogram, and to rise (for any particular substance) with a lowering of

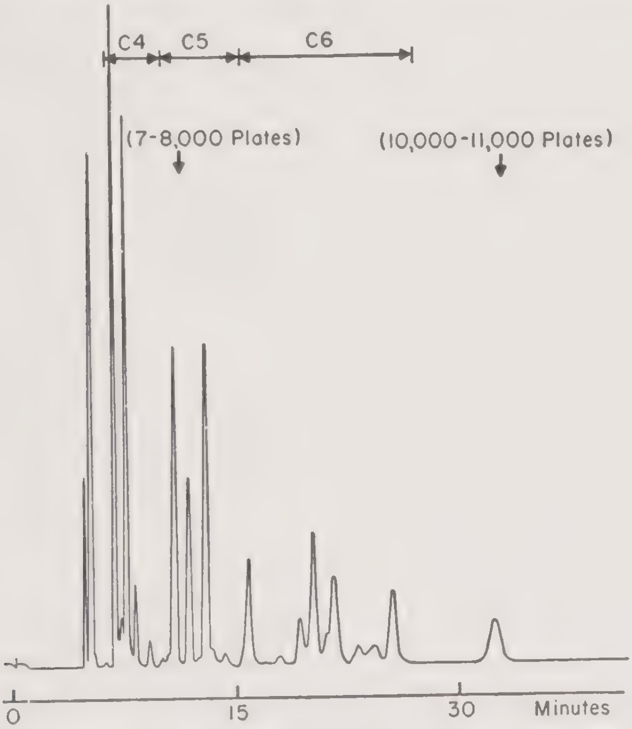

Fig. 2. Use of a column with large theoretical plate number. Petroleum fraction, 0°–75°C; 5% apiezon oil on C22 brick (100–200 mesh); 75% hydrogen, 25% nitrogen; column length = 25 feet; internal diameter = 3.6 mm; flow rate = 37 ml/min; 78°C. (Courtesy of Benzole Producers, Ltd., Watford, England.)

column temperature and hence increase of solubility. The slow diffusion can also be reduced by using a very thin liquid film. This effect is shown in Fig. 2, which has been kindly provided by Mr. Scott and Mr. Cheshire of Benzole Producers, Limited.

RETENTION TIMES

The retention time of the peak maximum can, by very simple corrections be made a physicochemical constant, characteristic of the vapor substance, the fixed liquid phase of the column and the temperature of operation. A retention time can thus be used directly for the identification of an unknown substance, just as the more familiar constants such as boiling point, melting points, or refractive index. Unlike these however, it is almost completely insensitive to the purity of the sample used, and for each substance one may use a variety of column liquids, each of which will provide a new characteristic time. These most valuable properties would seem to suggest that tables of retention times should be drawn up on some standard and commonly accepted basis. In Europe we have recently started on such a project in the "Gas Chromatography Discussion Group" (associated with the Hydrocarbon Research Group of the Institute of Petroleum). At a coming A. C. S. meeting,* we are presenting a paper, which has been written by Ambrose, Keulemans, and Purnell (*1*), containing some suggestions on how this compilation of data should be made. Briefly we consider that there are two kinds of data which are of importance:

(1) Relative Retention Times, i.e., retention times relative to certain internal standard vapor substances. These are obtainable with high precision and reliability with relatively little trouble, and they will serve for nearly all analytical purposes. The relative times should be corrected for the dead volume of the column, should be extrapolated to zero size of sample, and should if possible, be quoted at at least two temperatures; better still a graph of (the logarithm of the) relative retention times may be plotted against $1/T$.

The compilation of such times will obviously be greatly simplified if, at least at first, data is presented for a certain relatively small range of standard and reproducible column liquids. We have made some suggestions of suitable liquids (up to about 150° column temperature) and have succeeded in persuading some of the chemical firms to produce these liquids for us.

(2) Absolute Retention Volumes or Partition Coefficients. For a number of purposes, in particular the prediction of exact column performance, and for thermodynamic studies, it is desirable that absolute values of retention data should be published. The simplest manner of doing this is probably as V_g values (or specific retention volumes) as Littlewood, Price, and myself suggested (*7*) and as illustrated in Fig. 3. Specific retention volumes require accurate flow (and temperature) measurements, and a knowledge

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* *Editor's Note*: Held in New York City, September, 1957.

of the weight of column liquid. It should, however, be noted that conversion of relative retention times to absolute values only requires the determination of the absolute value(s) for the internal standard substance(s).

An alternative absolute value is provided by the partition coefficient, K, which requires in addition a knowledge of the density of the column liquid at the column temperatures. As V°_g and K are simply related by the equation.

$$V^\circ_g = \frac{273K}{T_c \rho_c}$$

(where T_c is the column temperature, and ρ_c the column liquid density at this temperature), it does not matter greatly which is given.

I hope very much that soon there will be discussion of this matter of the publication of standardized retention data in some detail, and perhaps some decisions which will enable all workers in the field to publish their results in such a manner as to be of the greatest assistance to others.

SEPARATION

Data plotted as in Fig. 3, (or relative retention times), can be used to decide the degree of separation which will be achieved with a particular

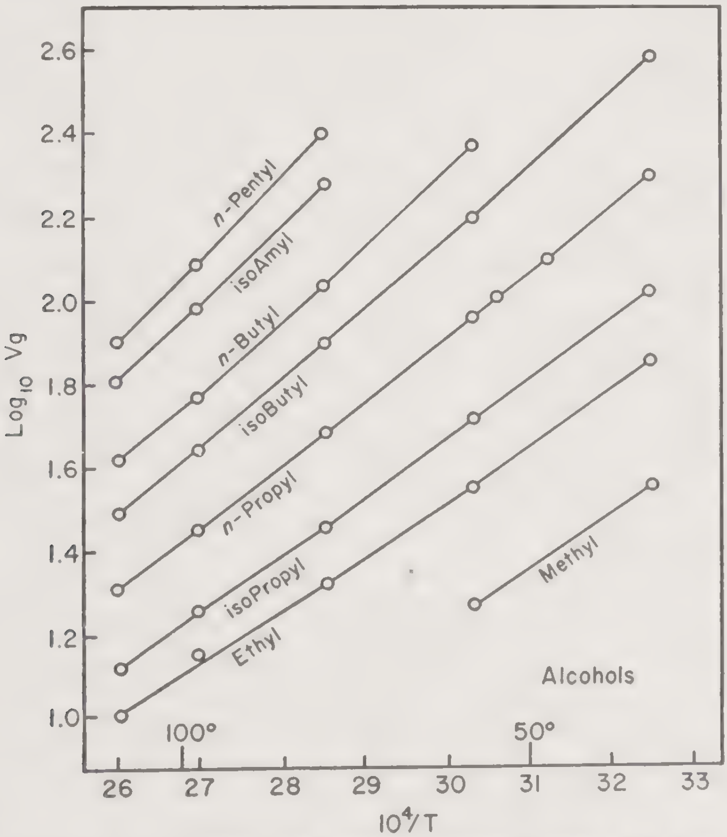

FIG. 3. Specific retention volumes for alcohols on Silicone 702 fluid. (Courtesy The Chemical Society, London.)

column liquid. Thus if we build and operate our column under conditions to give say 1,000 plates we shall require a separation factor of 1.16 for 99% separation, i.e., we shall separate two substances to this extent if they are $\log_{10}$ 1.16 or 0.065 apart on the $\log_{10} V°_g$ (or *RRT*) scale. Within an homologous series, the separation factor may vary from about 3.4 per CH_2 group at 20° to about 1.5 at 200° (e.g., with liquid paraffin as column liquid), but between e.g., positional isomers such as 2-Me-heptane and 4-Me-heptane, separation factor 1.04 on paraffin at 80°, this may be much lower (*5*). We then have to decide whether to construct a more efficient column so as to obtain more plates, or to change the column liquid so as to achieve a better separation factor. Commonly one adopts some compromise procedure.

Variation of Column Liquid

The variation of column liquid is of particular value for the separation of substances of different chemical type. One of the clearest examples is provided by an early paper of James (*4*), in which the oxygen atoms of polyethylene oxide (column liquid) were used to retard those amines which were able to form H-bonds with them. The marked retardation of primary amines, the lesser retardation of secondary amines, and the negligible retardation of tertiary (no active H-atoms) amines is shown up most clearly by a comparison of the retention times using polyethylene oxide as column liquid, with the retention times using paraffin as column liquid. This is shown in Fig. 4.

Now it is to be noted that the different active groups cause the retention times of the molecules containing them to fall on straight lines. This would seem to suggest that we are observing in each case a fairly constant free energy change of transfer from one column liquid to the other, which can be directly attributed to the active grouping. Gas chromatography thus provides a new way of testing for such groups. Instead of searching, as has become traditional organic practice, for a reagent to give a color reaction or characteristic smell (e.g., carbylamine test for primary amines) or, as more recently, for a suitable region of the spectrum for specific group absorption, we can now look instead for a suitable pair of differentiating column liquids.

The selective retardation of aromatics, napthenes, and unsaturated hydrocarbons on passing e.g., from paraffin to benzyl-diphenyl as column liquid is now also well known. It is however, I think not always so generally recognized that this change of column liquid also produces a useful relative retardation of straight chain aliphatic hydrocarbons with respect to branched chain aliphatic hydrocarbons. Thus the separation factor

n-heptane/2:2:4 trimethylpentane

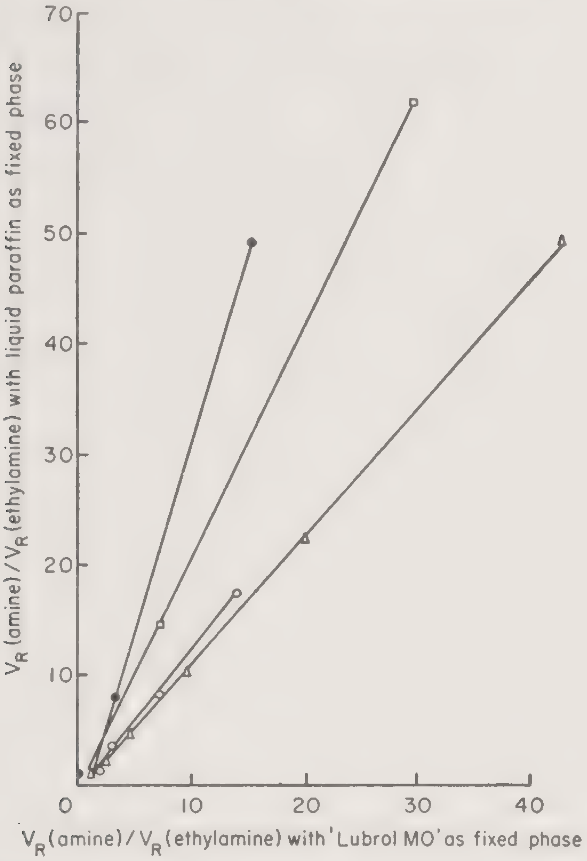

FIG. 4. The relationship between relative retention volumes (retention vol. of amine/retention vol. of ethylamine) for aliphatic amines on columns having stationary liquid phases of (a) liquid paraffin and (b) Lubrol MO, showing the relative speeding up of secondary and tertiary amines on changing from a solvent not allowing, to one allowing, hydrogen bonding. △-△, primary straight-chain amines; ○-○, primary isoalkylamines; □-□, secondary straight chain amines; ⊙-⊙, secondary isoalkylamines; ●-●, tertiary straight-chain amines. (After A. T. James, courtesy Cambridge University Press.)

at 80° is 1.08 with a liquid paraffin column, but 1.23 with a column of benzyl-diphenyl (*5*). The use of selective adsorbents may well prove useful for separations where structural rather than chemical differences are involved, for highly specific separations of this kind are well known in classical liquid-adsorbent chromatography. Molecular sieves provide a case in point.

More marked retardation of aromatics can be achieved by use of specific complexing with metal salts, for here the forces which can be used are considerably greater in magnitude than those encountered in mere solution. Thus while the separation factor

benzene/*n*-hexane

changes from about 1.6 on paraffin liquid to between 4 and 5 on an aromatic liquid such as benzyl-diphenyl or tetralin, we have found that it rises to 40 when a column of silver perchlorate (1.7 gm) dissolved in tetralin (4 gm) is employed.

USE OF METAL SALTS AS COLUMN LIQUIDS

More recently we have studied in my laboratory (*12*) the use of fused salts as column liquids. Our prime purpose in this work has been the study of inorganic complexing equilibria, as I shall describe later. We have used for the most part very short (and therefore, inefficient columns) because of the large retardations observed. However, the results are sufficient to show how these specific retardations can be used for analytical work, and the studies we have made may also be of interest as a model for work at really high column temperatures (above 500°C) where purely inorganic metal salts suggest themselves as satisfactory column liquids.

We have worked in particular with zinc stearate (M.P. 121–122°), copper stearate (M.P. 101°) and nickel oleate (M.P. 25–30°). These materials

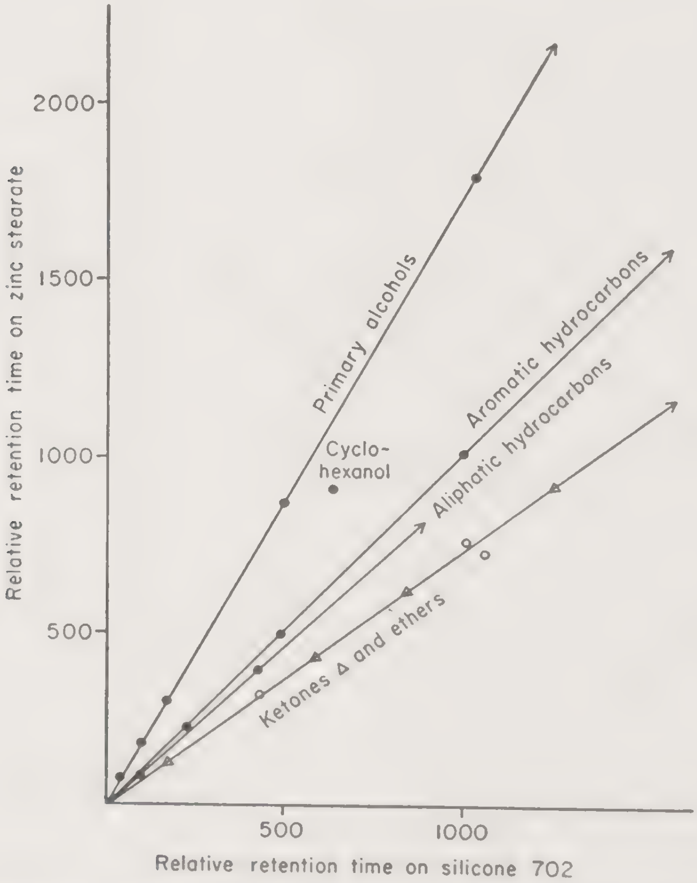

FIG. 5. Retention times on Silicone 702 and on zinc stearate columns at 156°C. (Relative to mesitylene as 1000.)

have proved to be quite stable over a six month period (e.g., zinc stearate at 157°). They are mixed with Celite in benzene solution and the benzene then evaporated off. As so prepared they have efficiency of about 3 to 4 plate per cm while a similar column of Silicone (702) fluid which we have used for comparison had an efficiency of 5 plates per cm. It is probable that this efficiency could be materially increased by a better mixing procedure. The columns have been run at temperatures above the melting points, although it is of interest to note that on one occasion due to an accident when the zinc stearate column was run 25° below its melting point it functioned as a separating column though with only about half the normal number of theoretical plates.

The selective retardations which can be achieved with such columns can be illustrated by the results in Fig. 5, where I have plotted the retention times on zinc stearate against retention times on silicone. All values have been referred to mesitylene as standard (retention time equal to 1000) a

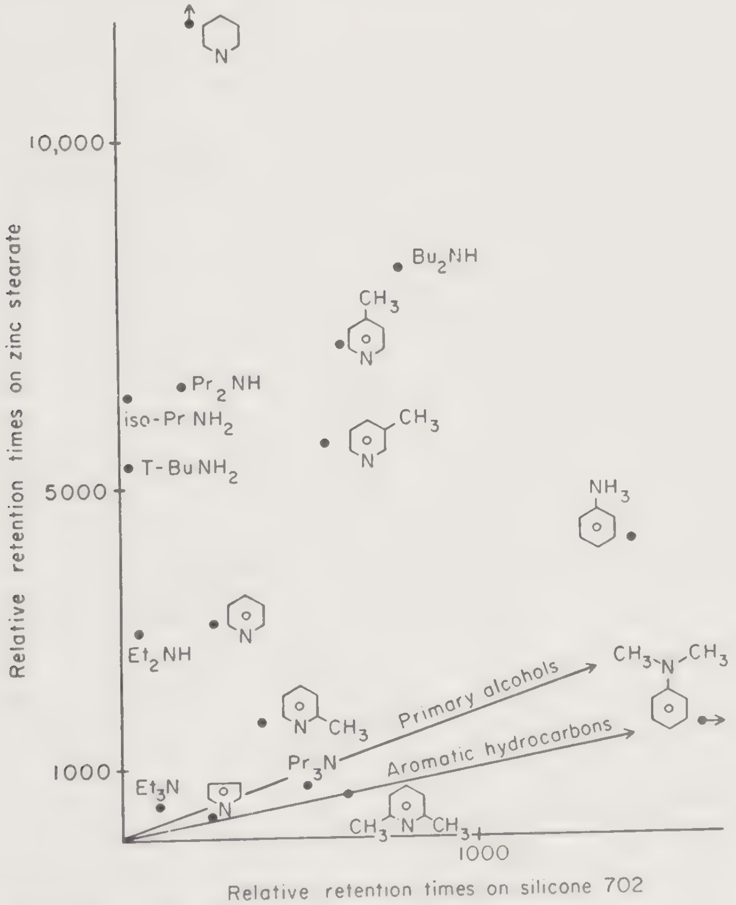

FIG. 6. Retention times on Silicone 702 and on zinc stearate columns at 156°C. (Relative to mesitylene as 1000.)

procedure which finds some justification in the fact that the heat of transfer of mesitylene from silicone to zinc stearate is only −0.1 kcal, a result which we obtained from absolute retention volume data made at two temperatures. It will be seen that relative to aromatic hydrocarbons, primary alcohols are retarded on the zinc stearate by a factor of 1.8, while ketones and ethers are accelerated by a factor of 1.4. On changing to copper stearate the primary alcohol retardation factor (again relative to aromatic hydrocarbons) is however, less than one (0.8), while for nickel oleate it is 3.1.

The largest retardation effects have been observed with amines. The results for zinc stearate are shown in Fig. 6. It will be seen that the retardation factors are now much more specific, but in general tertiary amines (e.g., tripropylamine 1.6) are less retarded than secondary (e.g., dipropylamine 38), which are less retarded than primary amines (e.g., isopropylamine 4,000). Some amines are so heavily retarded that they do not appear to move at all. Thus ethanolamine and ethylene diamine would seem to have retardation factors well in excess of 30,000. With copper stearate the retardation of amines is somewhat greater than with zinc stearate (e.g., pyridine has a retardation factor on zinc stearate of 12.5, and on copper stearate one of 17.5), except for the case of tertiary amines where the effect is the other way.

The manner in which these column materials may be used for separative purposes is illustrated in Fig. 7, which shows a separation of the picolines and 2:6 lutidine which is possible on a very inefficient (50 cm) zinc stearate column, but impossible on a silicone column with more than twice the plate efficiency. The most extreme case in this example is provided by

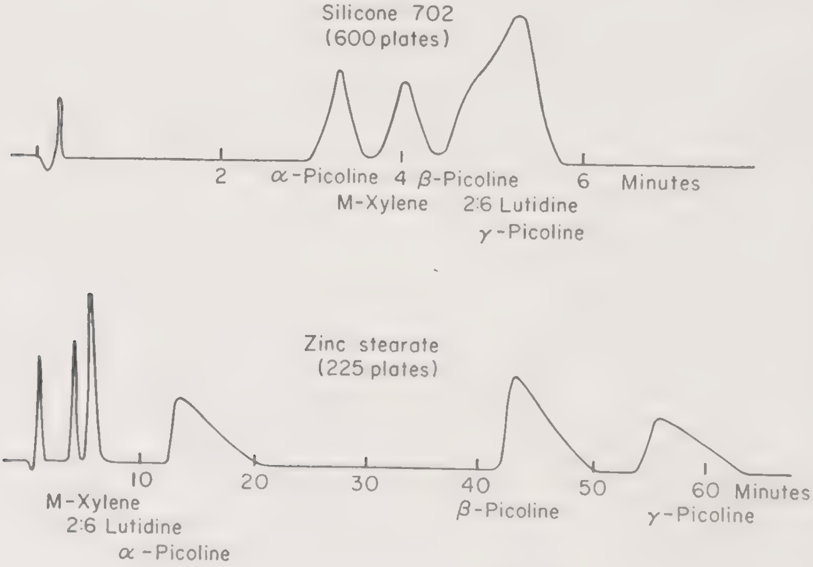

FIG. 7. Separation of picolines at 156°C.

γ-picoline and 2:6 lutidine, which would require for 99% separation a Silicone column of 250,000 plates (i.e., about ¼ mile long) but a zinc stearate column of only 4 plates (i.e., about 1 cm long). In the chromatogram of Fig. 7, the column has been deliberately overloaded to demonstrate the marked asymmetry which can then result, as a consequence of the competition by picoline molecules for the specific sites around the metal atom. With low sample sizes these peaks return to the more normal symmetrical shape. The assymetric peaks suggest however, that the system might well form a useful one for the application of displacement analysis (*12*) and might have the marked advantage over adsorbent columns in this connection that the active sites were much more uniform.

Physicochemical Equilibria

Gas chromatography makes use of processes of solution and adsorption to effect separations and analyses, but it is also a very valuable tool for the reverse process, namely the evaluation of physicochemical data connected with solution and adsorption (e.g., heats and entropies, and perhaps even diffusion rates) from analytical type experiments. As a technique it should have particular attraction to the physical chemist if the old story be true that while a physicist spends his time making very accurate measurements on impure substances, and the chemist spends his time making inaccurate measurements on very pure substances, the physical chemist only makes inaccurate measurements on impure substances. Even living down to this reputation he can do valuable work if he uses gas chromatography.

I would like to illustrate this type of application, by referring again to our work with metal salt columns, for this provides us with a new way of studying metal-complex equilibria. From measurements of absolute retention volumes it is a relatively simple matter to work out the free energies of solution of say an amine in the liquid metal salt. From relative retention times only, free energies of solution may be compared along a series. These free energies of solution are found to parallel very closely the (logarithm of the) basic dissociation constants of the aliphatic amines, but there are much greater free energies of solution in the case of amines like pyridine and the picolines which are capable of forming π complexes with the metal atoms than would be expected from this direct comparison of bonding strength to hydrogen. A similar situation has been found in the study of aqueous complexes by more traditional methods.

The effect of varying the metal is illustrated in Fig. 8. Here again we have a similar situation to aqueous complexing studies, where it has been found e.g., for ethylene diamine (R.H.S. of Fig. 8) that up to four active groups are accommodated more strongly around copper than around either nickel or zinc, but the fifth and sixth groups (K_3) less strongly owing

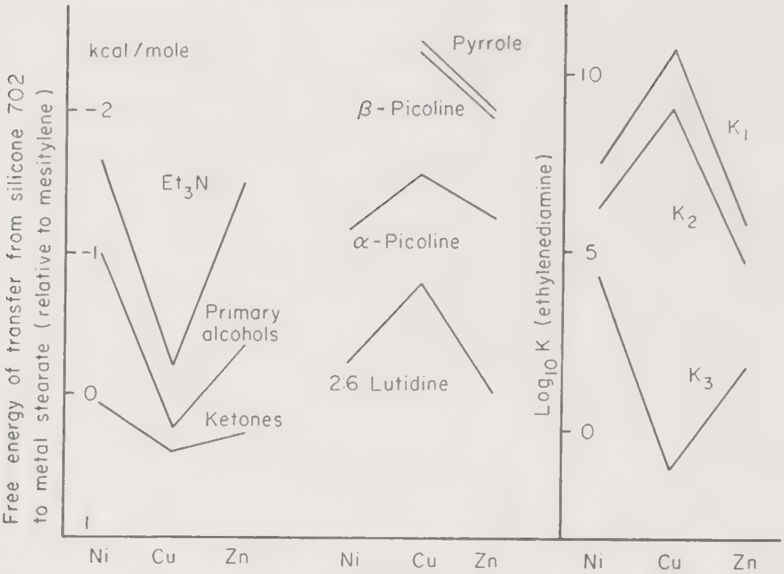

FIG. 8. Free energy of transfer from Silicone 702 to metal stearate. (Relative to mesitylene.)

to the Jahn-Teller effect. The L.H.S. of Fig. 8 shows how in our studies some substances follow the K_1, K_2 pattern and are presumably able to replace the CO group (of the stearate) from its coordination to the metal, while others are less strongly attached and follow the K_3 pattern.

INSTRUMENTATION

As I said at the beginning I have spent most of my time considering column processes, and that I do so is meant as a tribute to the excellence of the instrumentation which is now available commercially. While of course it is always very difficult to find a laboratory worker who would not wish to have an even better instrument than he has already, the available instruments do seem to provide all that is commonly required in the way of accurate flow control, precise and rapid injection systems, good column temperature control over a wide temperature range, and high sensitivity low-noise vapor detectors. It is, however, true that there still remain some problems where extremely high detector sensitivity is required. The most difficult separations require very small sample sizes and low operation temperatures and with thermolabile substances one may wish to work at temperatures so low that only very high sensitivity detectors can persuade them that they still are slightly volatile after all. High sensitivity ionization and discharge detectors have already been described by Ryce and Bryce (*11*), and by Harley and Pretorious (*3*). I would like here to draw attention to two recent British developments in the same direction. Dr. J. E. Lovelock (*8*) (National Institute for Medical Research, Mill Hill, London) has shown how a considerable (× 100) increase in sensitivity of the ionization type detector may be achieved by using argon as carrier gas. Argon atoms are easily raised to an excited, but non-ionized and hence non-conducting, state of about 11.5 volts. These excited atoms store up ionization energy and pass it on to the vapor molecules in collisions. Dr. R. C. Pitkethly (*10*) (British Petroleum Co., Sunbury-on-Thames) has develped a simple and improved discharge detector, in which the discharge tubes are made from ordinary neon indicator tubes. The instrument as at present developed has a noise level which corresponds to as little as one part of vapor in 50 million parts of nitrogen, which in other terms means that recognizable peaks are produced for example, with a sample containing 25% propane, 25% iso-butane, and 50% *n*-butane having a total gas volume of 10^{-6} ml. Using such a detector the maximum sample size is of the order 10–20 micrograms.

Commercial instrumentation has also provided satisfactory means for rapid quantitative analysis. The importance of this in applied chemistry is obvious, but to the academic it is of peculiar significance in the opportunity which it provides for the transformation of organic chemistry into an exact science. No longer shall we need to be satisfied with yields in an organic reaction quoted for one substance, and one particular set of operating conditions, but we shall hope for something of a mass balance with details of all the other products and the way in which the relative quantities of these may be changed with change of conditions. Perhaps a whole new field of organic chemistry may be found hidden away among the side reactions of organic chemistry, in the same way as a whole chemical industry was founded on the tar materials rejected in the manufacture of coal-gas.

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Discussion

Jones (*E. I. du Pont de Nemours & Co., Inc., Delaware*): I would like to ask you, Dr. Phillips, if you would care to comment a little more on your discharge detector. We have had a little bit of experience with this ourselves, and have found it to be nonlinear. In fact, it was approximately logarithmic, with an order of magnitude higher noise level than reported in the literature. In addition, it had the annoying property of reducing hydrocarbons to carbon.

Phillips: Perhaps Mr. Desty can offer some information on this point.

Jones: I was commenting, Mr. Desty, that we have been rather discouraged with our results on the electrical discharge detectors, having observed them to be logarithmic more than linear, and have not been as successful as you have been in achieving good signal-to-noise ratios. Our results have been about an order of magnitude poorer. We have also observed that with practically anything higher than C_2 the hydrocarbons are broken down to carbon, which deposits on the electrodes.

Desty (*British Petroleum Co., Ltd., England*): I brought along some specimen tubes from England. One of these has been used for about six months. You can see that though the tubes have large electrodes, the discharge occupies only about 25 per cent of the area. We have had no trouble at all with contamination of the electrodes, since they are being continually cleaned by the discharge. With regard to noise level, the presence of a positive column could be the source of the noise you have noted. Upon introducing hydrocarbon vapor into the discharge, the number of striations changes, and, as there is a small voltage drop across each striation, this can cause some trouble. Pitkethly has developed the use of the small indicator bulbs, which have the large electrodes separated by a very short distance (approximately 2 mm). In these tubes the positive column with the striations is completely eliminated. I remember that tubes of the type originally described by Pretorius did have a rather large noise level; larger than that he reported. In fact, that was one reason that Pitkethly abandoned this design and went to the small indicator bulbs.

Jones: I was working with helium. Perhaps this had some effect. Your work was with argon, was it not, Mr. Desty?

Desty: No, with both nitrogen and hydrogen.

Hinkle (*Monsanto Chemical Co., Texas*): With regard to your comment, Dr. Phillips, of the retardation of aromatics as compared to the naphthenes and paraffins, have you, in your experience, had occasion to try dinitrile-type compound in addition to your fused salts; for instance, adiponitrile?

Phillips: No, we have only used metal salts so far.

Hinkle: The reason I suggest this is that it is extremely selective for the aromatics and the data that you present on the tailing of the peaks is almost analogous in the dinitriles.

Lewis (*Tennessee Eastman Co., Tennessee*): With regard to your slide showing the plot of the retention times for the columns having different characteristics, if you plot logarithmically instead of linearly you avoid a crowding of points near the origin, and the lines are straight. The separation between the various homologous series, then, is fairly constant and the points representing homologs of each series are equally spaced.

Phillips: This has been done. Usually you obtain a series of lines cutting across one of the axes. There was no specific reason for the presentation used here.

DESTY: Two further thoughts have occurred to me about the discharge detector. With regard to linearity, the design developed by Pitkethly was linear over a sample size range of from 10^{-9} to 10^{-6} grams. Secondly, the formation of carbon may have been confused with sputtering of the electrodes. Using platinum, as Harley and Pretorius described, the electrodes quickly sputter a dark film onto the inside of the glass envelope, which leads to electrical leakage and additional noise. This may be an alternative explanation of the results that were obtained by the du Pont group.

JONES: On further reflection, I believe it is quite possible the nonlinearities that we have observed are due to the difference in carrier gas. We have an effect with helium that is not present with hydrogen or nitrogen. It may be that Mr. Desty has had this good result because of a fortunate choice of carrier gases. Regarding the formation of carbon (it is carbon—we have been able to grow carbon in filaments up to 2 mm in length), if any carbon does collect on the electrode, it forms a surface which can produce a discharge at a lower voltage; hence, the current tends to concentrate at these points. Thus, the nodules tend to build up into filaments. We have used platinum working surfaces, and have also used tungsten, with similar results. Perhaps there are other surfaces that have a lower firing potential and, hence, do not concentrate the current in this manner.

MACKAY (*Evans Research & Development Co., New York*): I was interested, Dr. Phillips, in your comments on the identification of compounds by their behavior in a column. My interest has been in the identification of compounds by using them as the substrate of a column. Have you had any experience in this direction?*

PHILLIPS: Yes, it's a perfectly feasible procedure. It means, of course, that you're restricted to some extent to things that are not particularly volatile, and of course, you have a mixture of substances—and you can't really distinguish between two mixtures. It also takes much longer to make a column than to run something through it. It is a nice technique to use to provide additional information on high molecular weight materials. Perhaps it might be important for the identification of polymers and similar materials.

* LATER COMMUNICATION: My reference to the identification of compounds by using them as the substrate of a column should have been amplified to state that the method involves characterizing an unknown by its ability to separate a standard mixture of volatiles under standard chromatographic conditions. For example the polyoxyethylene derivatives of sorbitan and related compounds (The Atlas Company's "Spans" & "Tweens") are very difficult to characterize as Span 20, 40, 60 etc. by chemical or spectroscopic methods, once beyond the stage of placing the unknown in the polyoxyethylene derivative class. If the possible knowns are made into substrates under standard conditions (this does not take long), and used to separate a standard mixture of esters or alcohols under standard conditions, a characteristic separation pattern may be obtained for each known and compared with that given by the unknown. I believe that this kind of chromatography can be a valuable adjunct to other kinds of analysis, especially where the unknown is a mixture or commercial product rather than a pure compound.

In fact, it is in just those cases where the unknown is a mixture that I believe best use can be made of this technique and accordingly I disagree with Phillips' views on this point.

CHAPTER VII

Precise Liquid Sampling in Gas Chromatography

D. W. CARLE

Scientific Instrument Division, Beckman Instruments, Inc.,
Fullerton, California

Gas chromatography can be the most accurate method for quantitative analysis of volatile compounds. It frequently is also the fastest and lowest cost means of analysis. The phenomenal growth of gas chromatography has paralleled recognition of these facts. But the high potential accuracy of this new technique has not always been achieved. The reason for this is that it is necessary to control precisely all of the variables of gas chromatography. In the first place, the analyst must have an excellent chromatograph. Particular attention must be given to control of temperature, carrier gas flow, and detector cell voltage. Even with perfect control of the chromatograph there remains the need for just as precise sampling as possible.

The approaches to liquid and gas sampling are quite different. Precise liquid sampling has generally been more difficult to achieve. One reason for this is the extremely small liquid volumes required. Normal samples range from 0.01 cc to 0.05 cc. In addition, it is desirable to sample to ±0.1% reproducibility in volume. This is only $\pm 10^{-5}$ cc for samples of 0.01 cc.

Several systems have been proposed for this problem. These have included micrometer driven syringes, liquid filled capillaries, or even the

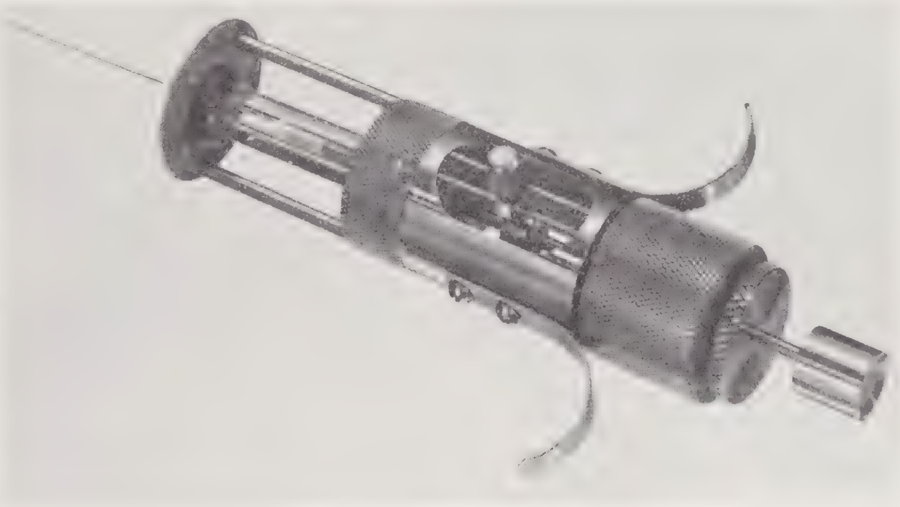

FIG. 1. Liquid sampler.

crushing of weighted ampoules in the chromatograph inlet. Without comparing these methods, it is apparent that each has disadvantages.

A positive displacement system was chosen in the design of the Beckman Liquid Sampler shown in Figs. 1 and 2. There are several inherent advantages in this design. Sample volume delivered is independent of sample viscosity, time-rate of addition is small and reproducible, plunger travel is relatively large for small samples, plunger travel is precisely reproducible, and a novel adjustment minimizes needle end effects.

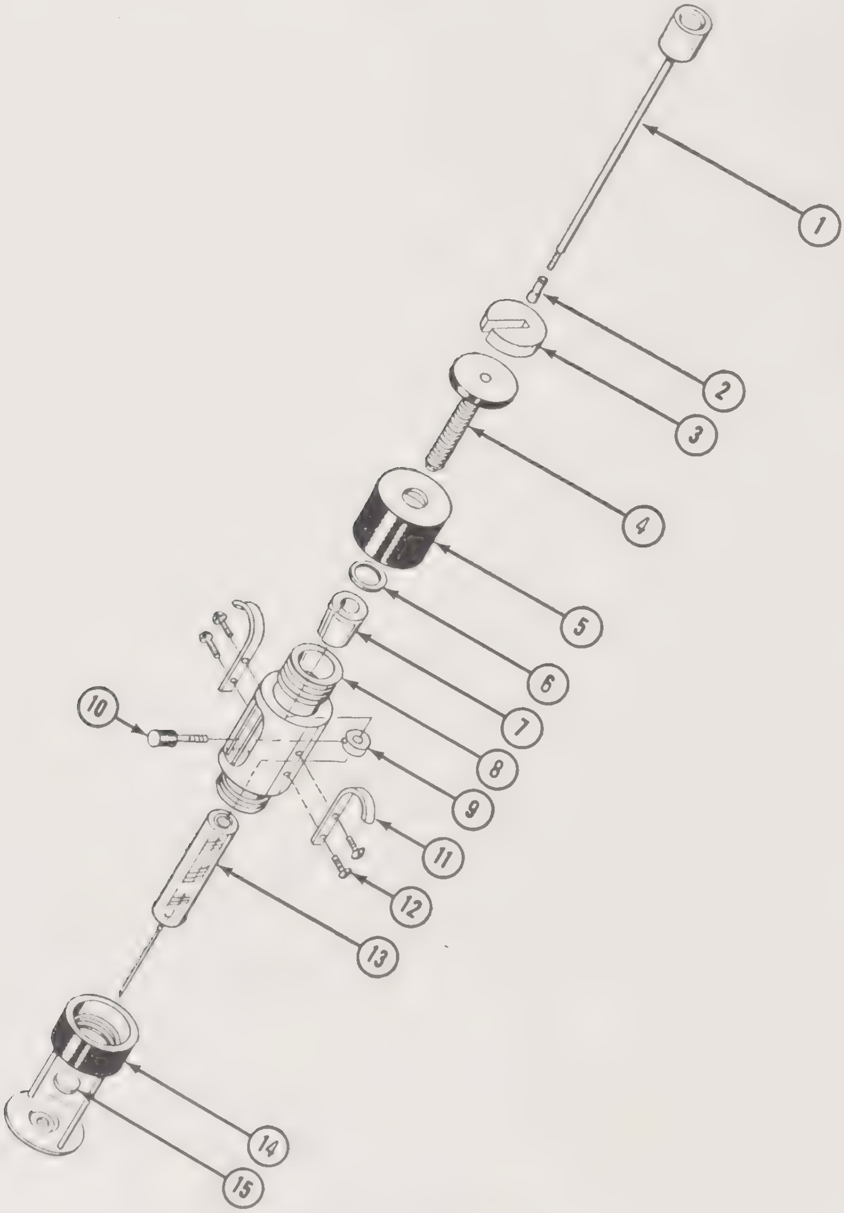

FIG. 2. Liquid sampler.

The problem of sample viscosity as well as plunger leakage against column pressure has been overcome by using a Teflon plunger (2) which is slightly larger than the diameter of the inside of the syringe (13).

Volume delivered is independent of the kind of liquid sample used. In use, the plunger rod (1) is driven forward with a rapid motion so that the sample is injected in a fraction of a second. Particularly where peak height is the basis for analysis this feature insures reproducible peak shape and hence reproducible peak height. Resolution is also improved by quick injection.

The volume of the syringe is approximately 0.06 cc and the plunger moves $\frac{1}{10}$ inch for each 0.01 cc. This relatively large motion aids in reproducing plunger travel for successive samples. Plunger travel is defined by movement between stops. To set plunger travel, one of several spacers (3) is placed between the head of the plunger rod (1) and the adjusting screw (4). The collar stop (9) is moved tightly against the threaded end of the adjusting screw (4) and locked in position with the set screw (10). The spacer is then removed and plunger travel is exactingly defined by this adjustment. The spacers are calibrated directly in volume, hence volumes are precisely determined and made reproducible by the spacer used.

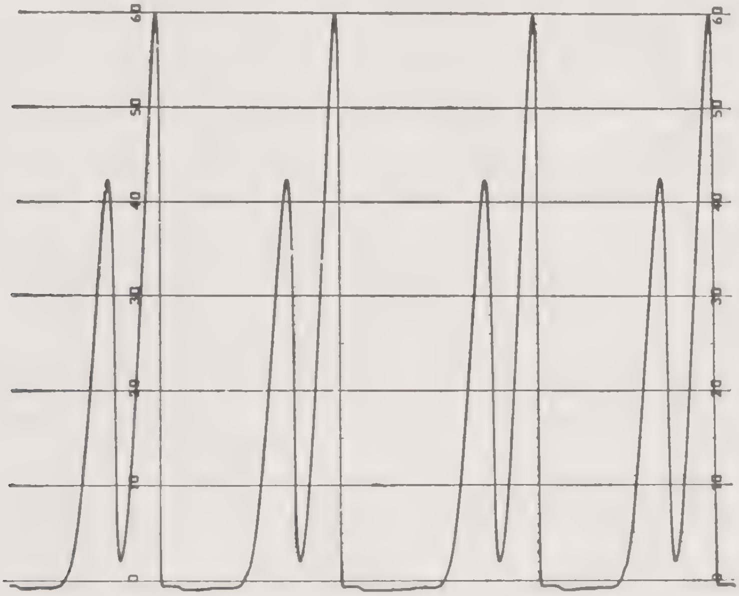

Fig. 3. Liquid sampler reproducibility.

00.2 cc cyclohexane & methyl cyclohexane

TEMP: 160° C

COLUMN: 6 ft Silicone

ATTEN: 100

FLOW: 80 cc/min

A novel feature of the design reduces needle end effects. The adjusting screw (4) thread fits into a split nylon cone (7) which can be tightened so that there is no backlash in the threads. The adjusting screw position has no effect on the volume delivered, hence it is possible to advance the plunger slightly and completely fill the needle just before injection. The diameter of the needle is as small as practical, and the total needle volume only 0.004 cc. This approach virtually eliminates needle end effects.

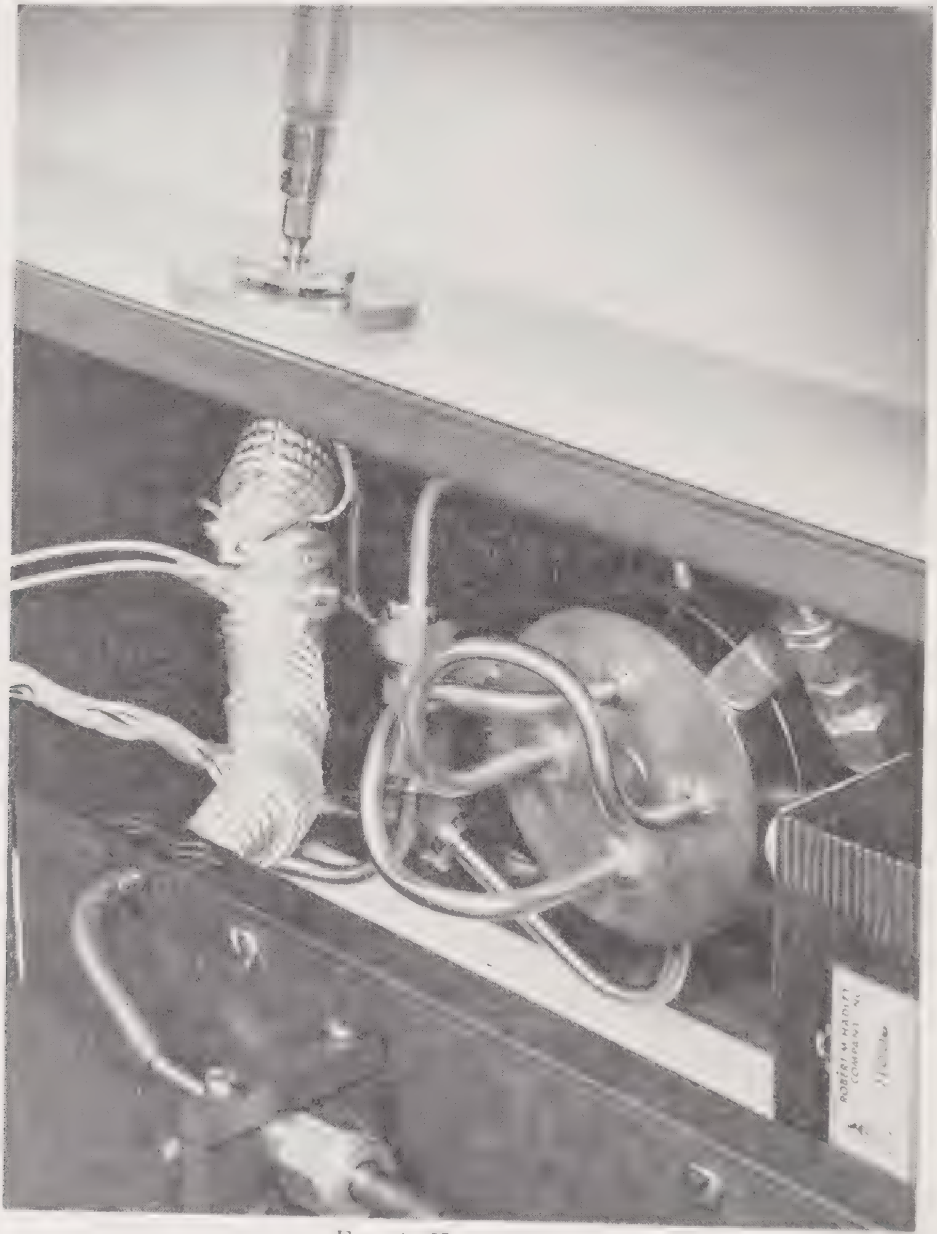

FIG. 4. Heated inlet.

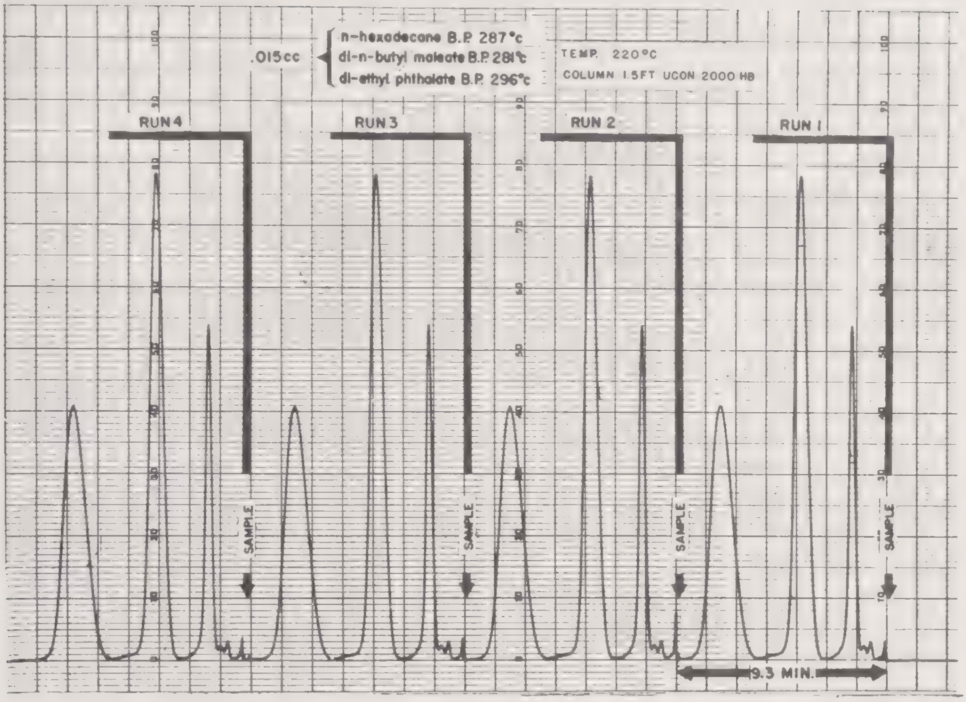

FIG. 5. Liquid sampler reproducibility.

The best way to measure the value of the design of any instrument is in terms of its performance. Figure 3 shows four successive samples of a relatively volatile mixture. Even at a column temperature considerably above the boiling point of the sample, reproducibility is ±0.2%. The chromatograph inlet plays an important role in getting this kind of reproducibility. Vaporization must be fast and reproducible. One way to accomplish this is to have a separate heater that keeps the instrument inlet above column temperature. Figure 4 shows the heated inlet of a model GC-2 chromatograph which was used for this work.

Viscous high boiling samples are a good test for any liquid sampling

TABLE I
LIQUID SAMPLER REPRODUCIBILITY
(0.015 cc Sample)

	Peak Height % Full Scale		
Run	*n*-Hexadecane B.P. 287°C	Di-*n*-butyl maleate B.P. 281°C	Di-ethylphthalate B.P. 296°C
1	54.2	78.4	41.1
2	54.0	78.3	40.9
3	54.1	78.4	40.9
4	54.0	78.4	40.9

device. Four successive runs of such a sample are given in Fig. 5. The elution order of hexadecane and *n*-butyl maleate is reversed by the column used. Table I is prepared from the data given in Fig. 5. Even better precision should be obtained with a larger sample.

The amount of data presented here is too small to give statistically derived limits of error. However, the results are typical of the reproducibility we have observed in this laboratory. Certainly, this system offers important improvement in the difficult problem of precise liquid sampling.

DISCUSSION

BLOCH (*Socony-Mobil Oil Co., New Jersey*): Is there any contamination from one sample to the next? In other words, is there any solution of the components in the Teflon plunger of your syringe?

CARLE: No, we have not had a bit of difficulty with this. If there is any solution in the Teflon, it is so small that we can't find it. I don't believe this presents a problem.

MARTIN (*England*): Against what pressure do you inject your sample?

CARLE: We have worked at column pressures of 30 pounds, and at this pressure we have not had any leakage problems. Just how much higher we can go I don't know.

DAL NOGARE (*E. I. du Pont de Nemours & Co., Inc., Delaware*): How did you fasten your needle to the glass barrel?

CARLE: This has a platinum tube that is sealed into the Pyrex, and the stainless is then sealed to the platinum. This removes the difficulty of a stainless-to-Pyrex junction, which is not too easy to achieve.

MADISON (*Shell Development Company, California*): Usually when we inject a sample we inject a little air along with the sample so that we get an air pip corresponding to the dead volume. When the syringe is loaded the air is removed.

CARLE: Well, we get this somewhat differently. We remove the air bubbles in filling the syringe, but there is usually enough dissolved air in the sample to give you a pip when running the chromatograph at full sensitivity.

CHAPTER VIII

The Analysis of Light Hydrocarbons by Gas-Liquid Chromatography

G. W. TAYLOR AND A. S. DUNLOP

Polymer Corporation Limited, Sarnia, Ontario, Canada

The use of gas-liquid chromatography (GLC) for the analysis of light hydrocarbons has been reported by a number of workers (*1*, *3*, *5–7*, *10–15*) who have used a wide variety of column packings. One of the most useful stationary liquids employed is dimethylformamide (DMF) (*3*, *9*, *10*, *11*, *15*) especially where a separation between isobutylene and *n*-butene-1 is required. For the analysis of complex light hydrocarbon samples where interference is encountered even with a DMF column, a combination column or a second analysis on a column having different separating characteristics has been suggested (*10*, *11*, *15*). In the present work, a 12-foot DMF column operated at 0°C is used for the analysis of C_4 hydrocarbon samples containing small amounts of C_3 and C_5 hydrocarbons and for the analysis of the product from a butylene dehydrogenation reactor. A second analysis on a 6-foot dinonyl phthalte (DNP) column operated at 40°C is used when necessary to correct for propylene and C_5 interference.

APPARATUS

Most of the work covered in this paper was done on the apparatus shown in Fig. 1. It consists basically of two separate analysis units, a control panel, and one recorder. Both analysis units are equipped with separate Gow-Mac T/C cells (Model TE-2) and separate remote control circuits.

The top analysis unit is fitted with an external 12-foot DMF column maintained at ice-water temperature in a Dewar flask. The air bath containing the carrier gas preheater, the detector, and the constant-volume sample inlet system is maintained at 30°C. The volume of the sample inlet system is nominally 5 cc and is of a design similar to that described by Harvey and Chalkley (*8*). The bottom unit is fitted with a 6-foot DNP column which is contained in the air bath along with the preheater coil, the detector, and the constant-volume sample inlet system. The air bath of this unit is maintained at 40°C.

The temperature of each air bath is controlled by a thermo-regulator and heat is supplied by an electric light bulb. Air is circulated by a small, vacuum-operated fan.

The recorder has a 0–15 mv slide wire and is connected to a 5-step

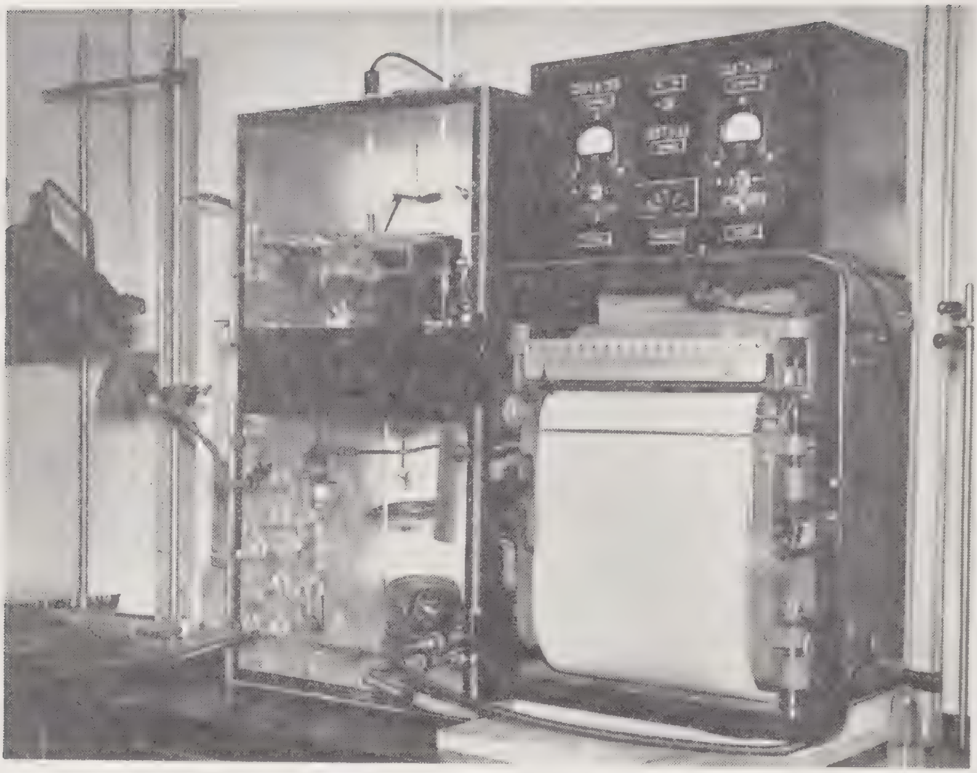

FIG. 1. Dual unit laboratory chromatograph.

attenuator capable of giving an effective range of 0–240 mv. The chart speed is 80 inches/hour and the pen requires three seconds for full scale deflection.

The work not done on this apparatus was carried out on a Beckman GC-1 instrument which was fitted with an external 12-foot DMF column immersed in an ice-water mixture.

SAMPLE INTRODUCTION

Gaseous samples are introduced from a transfer bulb using mercury or brine as displacing medium and no special precautions are necessary. However, for liquid light hydrocarbons care must be taken to obtain a representative sample, particularly when the sample contains components of appreciably different vapor pressures. As shown in Fig. 2, such samples are taken from the liquid phase of the container. They are allowed to vaporize very slowly at the needle valve so that bubbles appear at the exit of the system at a rate of 2–3 bubbles per second. Sample is allowed to flush through the system for at least two minutes and then the valve and stopcocks are closed. The exit stopcock is opened momentarily to ensure atmospheric pressure and the trapped portion is then introduced into the carrier gas by appropriate manipulation of the stopcocks.

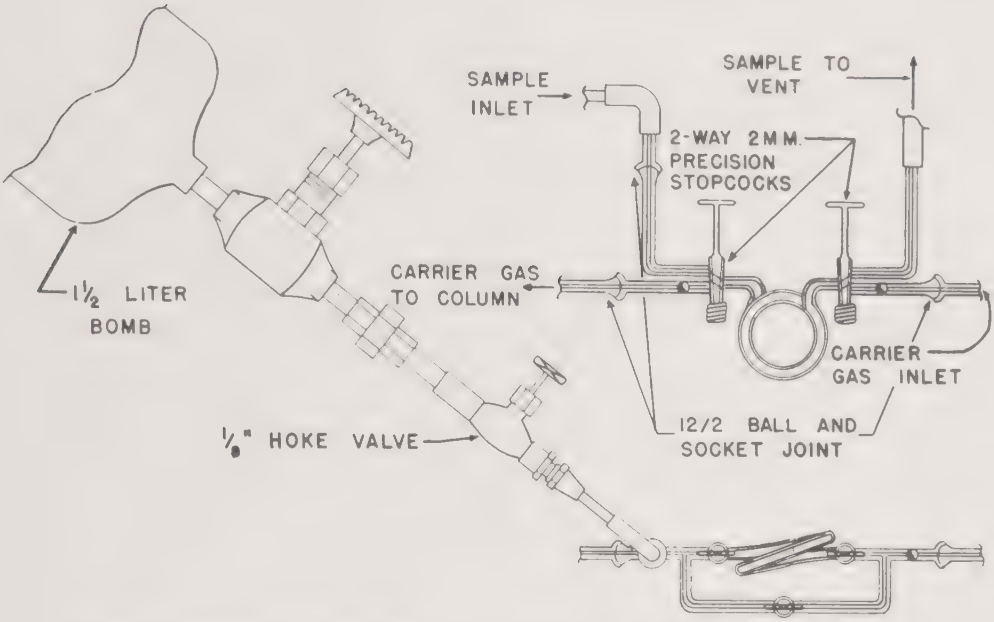

FIG. 2. Sample introduction system for laboratory chromatograph.

COLUMN PREPARATION

Columns are prepared using crushed C-22 firebrick for the solid support. A weight ratio of 40:100 of stationary liquid to solid support is used and the stationary liquid is added in an ether solution. The slurry is allowed to dry at a temperature no higher than 50°C with gentle stirring every 5–10 minutes. Excessive stirring must be avoided to prevent the formation of fines. When it has dried to its calculated weight, the mixture is passed over an 80-mesh screen and packed into previously cleaned and dried ¼ inch copper tubing. A 12-foot DMF column should contain about 40 grams of packing which should give a pressure drop of 8–10 lbs at a carrier gas flow rate of 60 cc/minute.

QUANTITATIVE INTERPRETATION OF CHROMATOGRAMS

Area measurements are probably the most commonly used for quantitatively interpreting a chromatogram. Although area per cent is closer to weight per cent than to mole per cent (*2*, *4*, *6*), it is not an accurate measurement of either. Calibration factors are therefore necessary and these are determined by analyzing either blends of known composition or pure components.

If area measurements are used, calibration factors are determined to correct the measured area of each peak so that area per cent gives either mole per cent or weight per cent directly. Likewise, if peak height measurements are used, the calibration factors are determined to correct the meas-

TABLE I

Comparison of Results Using the Same Calibration Factors for Different DMF Columns on Two Instruments

Component	Polymer Instrument		Beckman GC-1	
	Column A	Column B	Column A	Column C
A. Results Calculated from Areas				
Isobutane	3.5	3.3	3.2	3.2
n-Butane	14.2	14.0	13.8	13.9
n-Butene-1	16.7	16.7	16.6	16.5
Isobutylene	6.9	7.0	7.1	6.7
trans-Butene-2	21.8	22.0	22.2	22.2
cis-Butene-2	19.1	19.2	19.3	19.7
Butadiene	17.8	17.8	17.8	17.8
B. Results Calculated from Peak Heights				
Isobutane	3.5	3.3	3.3	3.0
n-Butane	13.1	13.2	14.2	13.9
n-Butene-1	16.5	16.6	16.8	16.4
Isobutylene	6.9	6.8	6.9	6.8
trans-Butene-2	21.8	21.9	22.0	22.5
cis-Butene-2	19.2	19.2	19.0	19.6
Butadiene	19.0	19.0	17.8	17.8

ured peak height so that peak height per cent gives either mole percent or weight per cent directly.

An indication of the consistency of DMF calibration factors for different columns on two instruments is given in Table I. This table shows that when using area measurements, essentially the same results are obtained on different columns in different instruments. This means that area calibration factors need be determined only once.

When using peak height measurements, essentially the same results are again obtained with different columns in the same instrument. However, significantly different results are obtained with the two instruments. This is probably due to peak heights being more dependent upon operating conditions than are areas. (*3*, *11*)

Deterioration of DMF Columns

The DMF columns have a finite life and their performance gradually deteriorates as illustrated in Fig. 3. This deterioration takes the form of shorter elution times and decreased resolution between butene-1 and iso-

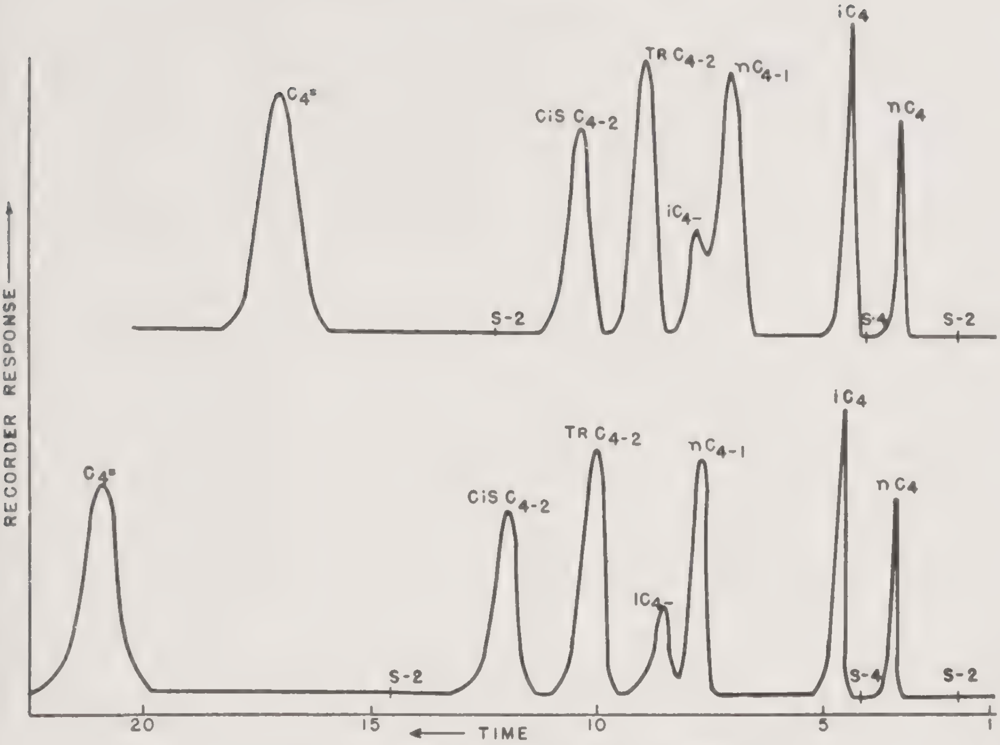

Fig. 3. Comparison of new and old 12-foot DMF columns.

butylene. The main cause of this deterioration is probably gradual loss of DMF even when operating the column at 0°C.

Calibration factors for both areas and peak heights appear to hold over the life of a column since no significant difference in results is obtained when analyzing a standard seven component C_4 blend on a new and on an old column.

The useful life of a DMF column is dependent upon the manner in which it is used. Failure to keep the temperature at 0°C whenever carrier gas is passing through the column will appreciably shorten its life. Our experience has been that a 12-foot column will last for up to 16 weeks and that it can be used for up to 400 analyses.

PRECISION OF RESULTS ON DMF COLUMNS

An indication of the precision of C_4 results obtained with a DMF column is given in Table II. These precision data were obtained on a Phillips Blend #37 which was analyzed twice per day for 18 days over a three-month period. The results were calculated by three methods: areas, peak heights, and the product of peak height times retention time. The precision is stated in terms of standard deviation within a day and standard deviation over an extended period. From these data it appears that the peak height

TABLE II

Comparison of Precision Obtained by Different Calculation Methods

Column = 12-foot DMF column at temp. of 0°C
Sample = Phillips Blend #37
No. of runs = 2 per day for 18 days over a 3-month period

Component	Conc. Mol. %	Standard Deviation within Day			Standard Deviation Different Days		
		Area	Pk. Ht.	Pk. Ht. × Ret. Time	Area	Pk. Ht.	Pk. Ht. × Ret. Time
Isobutane	3.3	0.08	0.06	0.06	0.08	0.07	0.09
n-Butane	14.1	0.12	0.06	0.07	0.16	0.16	0.21
n-Butene-1	16.7	0.20	0.12	0.12	0.20	0.12	0.14
Isobutylene	7.0	0.10	0.07	0.07	0.11	0.09	0.08
trans-C_4^{-2}	22.0	0.14	0.11	0.10	0.21	0.14	0.17
cis-C_4^{-2}	19.0	0.21	0.20	0.20	0.25	0.22	0.23
Butadiene	17.9	0.19	0.12	0.14	0.24	0.23	0.23

method of calculation gives the most precise values at least for a sample which has a fairly constant composition.

Separations Achieved on DMF Columns

The elution times obtained for a number of materials on a 12-foot DMF column operated at 0°C with a helium flow of 60 cc/minute are shown in Table III. The peaks for ethane and ethylene are sufficiently sharp that resolution is obtained even though elution times differ by very little. Some difference is shown for isobutane and propylene. On a new column no resolution is obtained between these components. However, on a column which has been in use for about a week, partial resolution is obtained if these two components are present in about equal amounts with their total concentration being about 3% or less. In the C_5 range, isopentane is not resolved from isobutylene, *n*-pentane appears in the *cis*-butene-2 area, and pentene-1 comes off with butadiene.

Part of a chromatogram of a C_4 sample containing light ends is shown in Fig. 4. This is a chromatogram of a butylene dehydrogenation reactor product when using a chrom-alumina catalyst. The only component not shown here is butadiene which would be off to the left of the illustration. This chromatogram shows the CO/C_1 peak, the split between ethane and ethylene, propane, CO_2 and propylene. No isobutane is present in this sample so that isobutane-propylene interference is no problem. Approximate concentrations illustrated are 11% $CO + C_1$, 1.5% ethane, 3.5% ethylene, 0.3% propane, 0.2% CO_2, and 3.5% propylene.

TABLE III

ELUTION TIMES ON A 12-FOOT DMF COLUMN

Column Temp. = 0°C Helium Flow = 60 cc/min.

Component	Elution Time–Minutes
Air	1.2
Ethane	1.6
Ethylene	1.8
Propane	2.5
Carbon Dioxide	3.1
Isobutane	3.6
Propylene	3.8
n-Butane	4.9
n-Butene-1	8.2
Isobutylene, Isopentane	9.1
trans-Butene-2	10.7
n-Pentane	11.8
cis-Butene-2	12.5
3-Methyl-butene-1	13.6
Ethyne	15.3
Pentene-1	20.2
Butadiene 1:3	21.7
2-Methyl-butene-1	24.3
trans-Pentene-2	25.2
cis-Pentene-2	27.6
2-Methyl-butene-2	33.2
Propyne	33.5
Butadiene 1:2	35.4

Part of a chromatogram of a C_4 sample containing small amounts of seven C_5 hydrocarbons is shown in Fig. 5. The total C_5 content of this sample was 0.8 mole %. The isopentane is included in the isobutylene and the *n*-pentane in the *cis*-butene-2. The 3-methyl butene-1 at 0.16 mole % is separated although the pentene-1 is included in the butadiene. The next peak represents 0.16% 2-methyl butene-1 while the last peak shown is 0.08% of *cis*-pentene-2. This sample contained 0.11% of 2-methyl butene-2 which was not detected.

COMBINING ANALYSES FROM A DNP COLUMN WITH THOSE FROM A DMF COLUMN

In order to correct for such C_5 interference and also to obtain a split between propylene and isobutane, a second analysis is carried out on a 6-foot DNP column operated at 40°C. The elution times obtained for a number of substances on this column using a carrier gas flow rate of 60 cc/minute are given in Table IV.

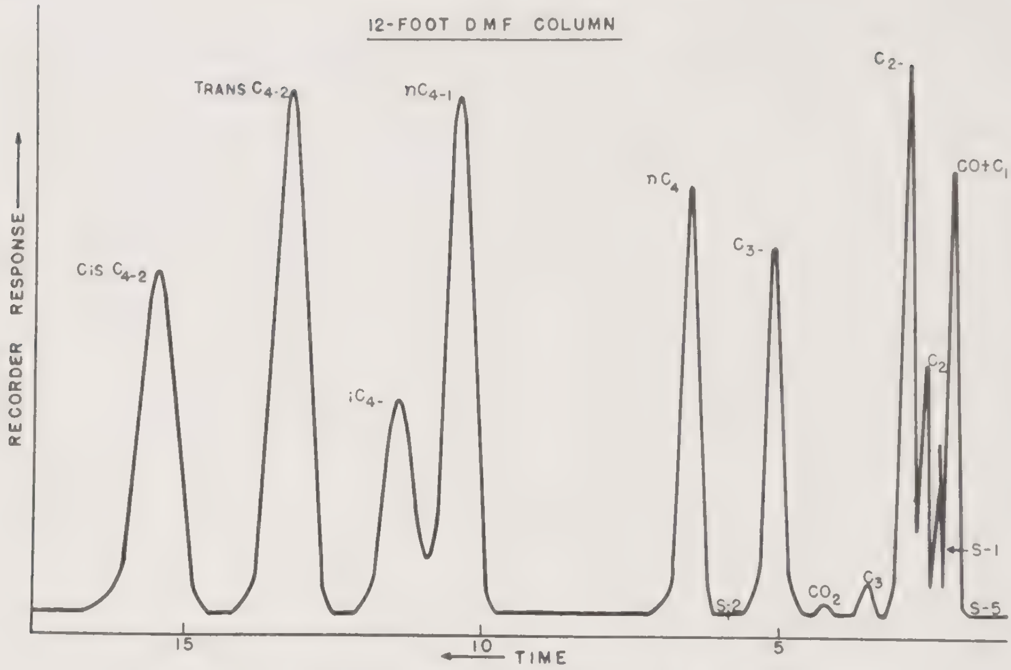

FIG. 4. C_4 Hydrocarbon sample containing a light fraction.

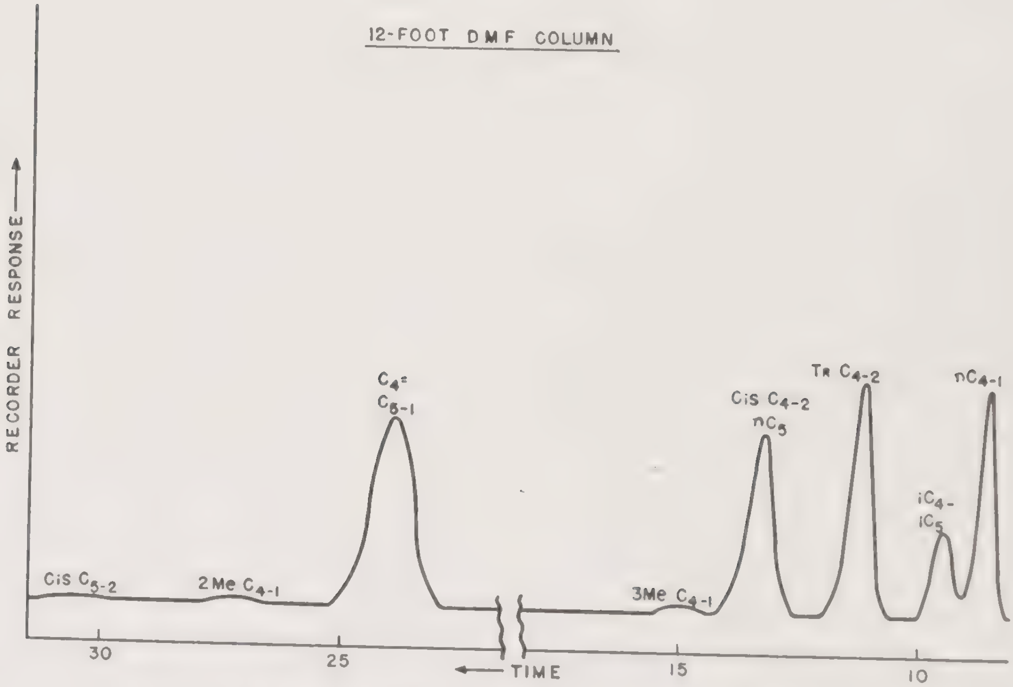

FIG. 5. C_4 Hydrocarbon sample containing 1% C_5.

TABLE IV

ELUTION TIMES ON A SIX-FOOT DNP COLUMN

Column Temp. = 40°C Helium Flow = 60 cc/minute

Component	Elution Time–Minutes
Air	0.6
Carbon Dioxide, Ethane, Ethylene	0.8
Ethyne	0.9
Propane, Propylene	1.2
Isobutane	1.9
Propyne	2.3
n-Butane, *n*-Butene-1, Isobutylene	2.5
trans-Butene-2, Butadiene 1:3	3.5
cis-Butene-2	3.9
3-Methyl butene-1	5.0
Butadiene 1:2, Isopentane	5.3
n-Pentane, Pentene-1	6.8
2-Methyl butene-1	7.5
Pentene-2	8.7
2-Methyl butene-2, Isoprene	9.8
Pentadiene 1:3	12.5
Cyclopentane, Cyclopentene	14.2

This table shows that propane and propylene appear as one peak with no interference from any of the C_4's. Also the C_5's are eluted after the C_4's with the only interference being between isopentane and butadiene 1:2. If butadiene 1:2 is present in a sample, it is obtained as a separate peak on the DMF column. Normally, everything after the C_4's is considered to be C_5 or heavier.

From the times shown, it is seen that a rapid analysis is obtained on such a column. Generally it is sufficient to run the chromatogram only to the 2-methyl butene-2 peak.

A typical run on a DNP column is illustrated in Fig. 6. This represents a C_4 sample containing 0.9% total C_3 and 0.8% total C_5, the C_5 being made up of seven components. This chromatogram shows the C_3 peak, the C_4's indicated by two off-scale peaks, and the C_5's. The first C_5 peak contains 3-methyl butene-1 plus isopentane. The second peak contains the *n*-pentane, the pentene-1, the 2-methyl butene-1 and the *cis*-pentene-2, with partial resolution shown for the *cis*-pentene-2. The final peak contains the 2-methyl butene-2.

As indicated in Fig. 6, the DNP analyses are run at maximum sensitivity for all components providing the C_3 and C_5's remain on scale. This requires a different type of calibration than used on DMF columns. Area

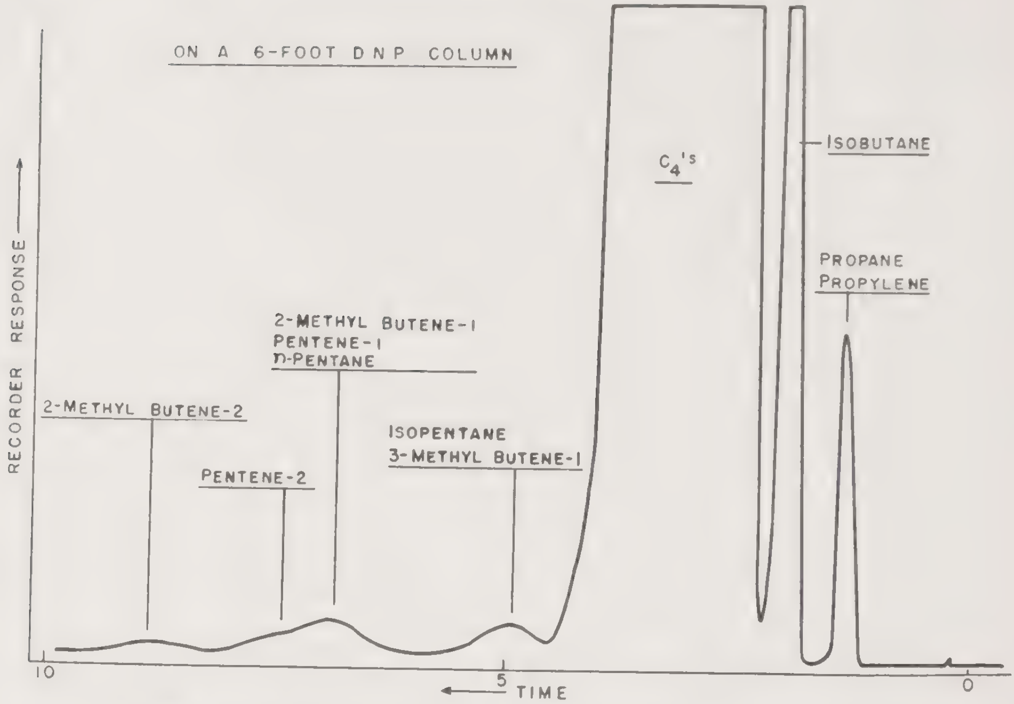

FIG. 6. C_4 Hydrocarbons containing 1% C_3 and 1% C_5.

measurements only are used and factors are derived to convert area directly to mole % concentration. This requires using a constant volume sampling device and the factors are obtained by analyzing blends containing a known concentration of C_3 and C_5. The standard deviation of results obtained by this method is estimated to be 0.08 mole % for 1% total C_3 and 0.09 mole % for 1% total C_5.

An indication of the accuracy obtained by combined analysis is given in Table V. Blend #1 illustrates a C_4 sample containing both propane and propylene. On the DMF run, the propane is obtained as a separate peak while the propylene is lumped with isobutane. Total C_3 is obtained on the DNP column and the difference between this and propane gives propylene, and the isobutane is then corrected by this amount.

Blend #2 illustrates a C_4 sample containing C_5's. On the DMF column, only 3-methyl butene-1, 2-methyl butene-1, and pentene-2 showed as separate peaks. The DNP column gave three C_5 peaks as was illustrated in Fig. 6. The combination of these two analyses allowed a correction to be made to the C_4's for C_5 interference and separate values were obtained for all C_5's except *n*-pentane and pentene-1.

Blend #3 was a five component C_4 sample containing 12% isopentane and 5% *n*-pentane. This is considerably above the C_5 content normally encountered and yet the results are still reasonably good. Some of the

TABLE V

Accuracy of Combined Analyses Using a 12-Foot DMF Column and a 6-Foot DNP Column

Results are from single determinations and area measurements

Component	Blend #1 Mole %		Blend #2 Mole %		Blend #3 Mole %	
	Exptl.	Dev. from Theor.	Exptl.	Dev. from Theor.	Exptl.	Dev. from Theor.
Propane	0.47	+0.02				
Propylene	0.42	−0.03				
Isobutane	3.2	—	3.2	−0.1	19.9	−0.7
n-Butane	13.9	−0.1	14.3	+0.3	41.7	+0.3
n-Butene-1	16.7	+0.1	16.5	+0.1	1.1	—
Isobutylene	7.0	+0.1	6.8	−0.1		
trans-Butene-2	21.6	−0.2	21.6	−0.3	3.2	—
cis-Butene-2	19.1	+0.2	19.1	+0.2	16.8	+0.6
Butadiene 1:3	17.6	−0.1	17.7	—		
3-Methyl butene-1			0.17	+0.01		
Isopentane			0.11	+0.04	12.2	−0.1
n-Pentane			0.16	−0.07	5.1	−0.1
Pentene-1						
2-Methyl butene-1			0.16	—		
Pentene-2			0.09	+0.01		
2-Methyl butene-2			0.09	−0.02		

error here is due to difficulty in obtaining a representative aliquot of a sample of so high a C_5 content.

Conclusion

A 12-foot DMF column operated at ice temperature is an extremely useful column for light hydrocarbon analyses. It gives excellent resolution, particularly for the C_4's. It provides a fairly rapid analysis since running time for most samples is of the order of 25 minutes. This results in a rapid routine method especially if peak heights are used for calculation. Although area measurements are more suitable for samples having a wide range of composition, peak heights are satisfactory for samples having a fairly constant composition.

Where interference from propylene and C_5's is encountered, a supplementary analysis on a 6-foot DNP column at 40°C provides sufficient information to correct for this interference. This supplementary analysis requires an additional 10–15 minutes.

The use of two separate columns as described is preferred to the use of a single combination column. In this way the good resolution of the DMF column, particularly for *n*-butene-1 and isobutylene, is maintained, and more information is obtained than from a single run.

Acknowledgment

The authors wish to express their appreciation to Polymer Corporation Limited for permission to publish this report.

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DISCUSSION

CHIN (*Lummus Company, New Jersey*): I notice in your sampling of the liquid phase (I assume this is an LPG gas) that you only have a series of two valves leading to your sample system. Aren't you afraid that you will obtain some fractionation, rather than a representative sample?

TAYLOR: Fractionation will take place unless the sample is taken at a slow enough rate. This is why we specified that the sample should be bubbled through at a rate no faster than two to three bubbles per second. At that rate there has been no indication of any fractionation taking place.

CHIN: Therefore, I would assume it would vary from operator to operator if the different operators are not careful in using the correct bubble rate.

TAYLOR: This will certainly take place on the first couple of analyses that a new operator makes, but we have found that with a fairly short amount of training there is no problem of agreement of results between different analyses.

CHIN: I believe you are familiar with the book on "Analysis of Light Hydrocarbons" published about six years ago. In this book a system was proposed for sampling LPG gases from the liquid phase. Briefly, it states that a liquid portion is trapped between two valves and then permitted to expand into a chamber. The required volume of this chamber is determined from a preliminary calculation of the dew point pressure of the LPG sample. This would insure that the sample was completely vaporized in the chamber. The now gaseous sample can then be introduced into the analysis instrument.

TAYLOR: Yes, this is so. I believe it was also stated there that you can take representative samples directly from the liquid phase, using either very rapid vaporization or very slow vaporization. The data I presented was obtained with three operators.

BLOCH (*Socony-Mobil Oil Co., New Jersey*): Was your support Celite or brick? And what was the useful life of your dimethylformamide column at 0°C. before the emergence picture changed?

TAYLOR: The answer to your first question is brick. As far as life is concerned, we ran them for up to 16 weeks, or up to 400 analyses.

CHAPTER IX

Analysis of Light Ends on Saturate Naphthas, Using Gas Chromatography

W. A. DIETZ

Esso Research and Engineering Co., Linden, New Jersey

Fuels produced by various refining techniques contain varying small amounts of ethane, propane, and the lighter hydrocarbons. Generally, octane ratings are reported on a C_5^+ basis, even though the octane measurements are run on the total sample. Means must therefore be provided for correcting for the contribution due to the C_4 and lighter gases present.

Prior to the advent of gas chromatography the analysis of these light ends was done by low temperature distillation and mass spectrometry. This was time consuming and not always accurate. Gas chromatography has provided a simple and rapid means of accurately measuring the individual compounds, ethane through pentane inclusive. The method has been widely adopted for measuring light ends in olefin-free naphthas. Saving in time over previously used analytical methods is over two hours per sample, with equal or greater accuracy of results.

A column of silicone fluid on Celite or firebrick will completely resolve ethane, propane, iso- and *n*-butane, and iso- and *n*-pentane from a total gasoline boiling range mixture containing these compounds. The test requires calibration with standard samples. Since these components are eluted from the column rather rapidly, it is convenient to use peak height for calibration, rather than integrated peak areas. Over narrow limits, peak height is a linear function of the volume of sample. Hence, it is only necessary to calibrate with a concentration close to that of the concentration believed to be present in the sample.

After the chromatogram has been developed through *n*-pentane, the C_6 and heavier components can be removed from the column by reverse flushing of the sample charge. This procedure materially reduces the overall running time. Figure 1 shows how a four-way valve can be installed to provide reverse flushing. The solid lines show the path of sample and helium with the valve in the normal running position. On reverse flushing, helium follows the dotted path and the material is ejected from the column to the atmosphere. Reverse flushing requires slightly more time than was taken to develop the sample.

This system has proven to be very useful. If an incorrect sample, or the wrong amount of the sample has been charged, it can be quickly removed by back flushing instead of waiting for it to be eluted in the regular manner. This valve is being included as standard equipment by at least one instrument manufacturer.

The column can be calibrated in either of two ways. One method is to calibrate using each pure component at several concentrations. For the gases (C_2 and C_3), this would be done by using two or three different volumes of each gas, measuring the peak height each time. The gas volume can be converted to equivalent volume of liquid sample. Calibration for

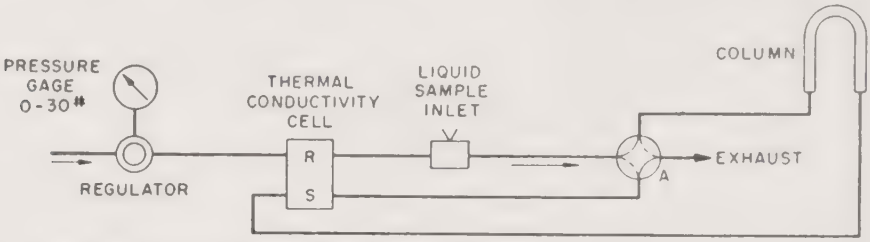

FIG. 1. Installation of reverse flushing valve. A 4-way valve Teflon plug (Republic Manufacturing Co., Cleveland, Ohio; Model 310-6-1/8). Valve position: Solid lines are running position. Dashed lines are reverse flushing.

TABLE I

LIGHT ENDS ON SATURATE NAPHTHAS BY GAS CHROMATOGRAPHY

Operating Conditions:	
Column	2 Meters × ¼″ O.D.
Packing	35 Wt.% Silicone fluid on Celite 545
Temperature	75°C.
Carrier Gas	Helium at 10 psig
Flow Rate	75 ml/min
Recorder	0–5 MV
Recorder Speed	30″/hr
Sample Size	0.0100 ml (liquid)

TABLE II

STANDARD BLEND

	Liquid Vol.%
Ethane	0.03
Propane	1.00
Isobutane	2.00
Normal Butane	3.00
Isopentane	5.50
Normal Pentane	4.40
Balance	250–300°F. Virgin Naphtha

isobutane through *n*-pentane can be done by charging liquid samples in a chilled pipette.

The second method, which is simpler, requires only one run since a standard sample is prepared using all components in known concentrations. Calibration with this blend is done once each day. Little variation has been shown from day to day (generally less than 1 %).

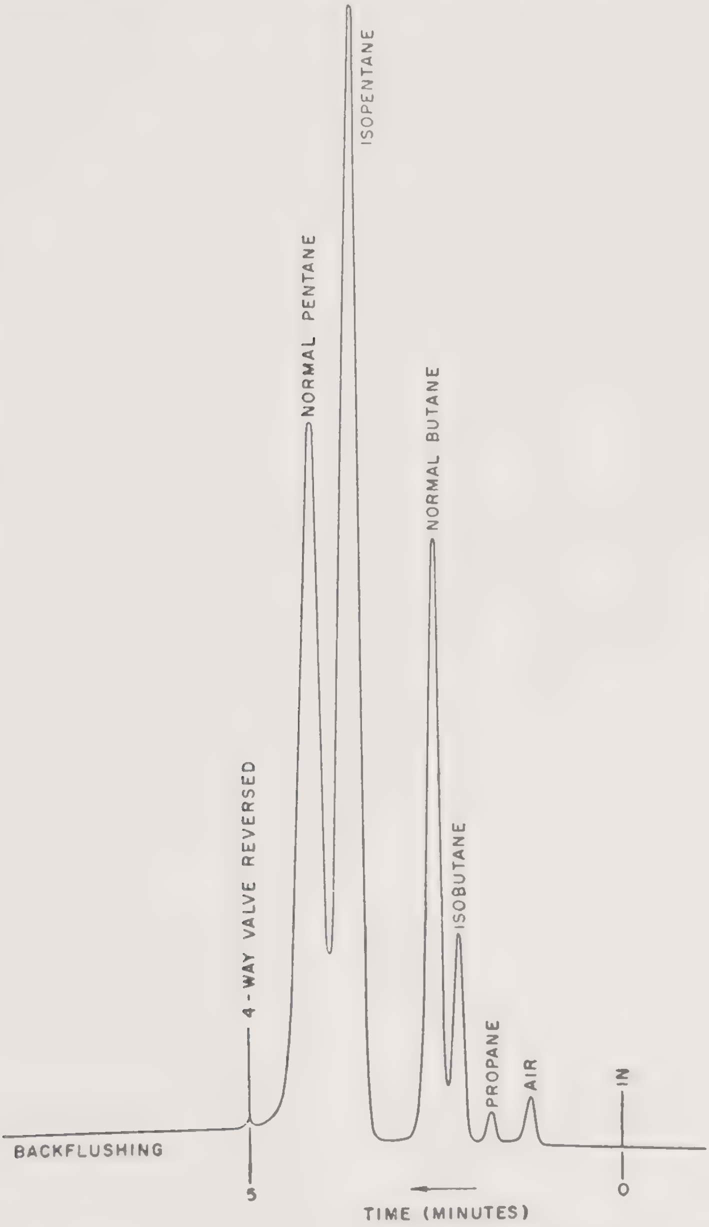

FIG. 2. Chromatogram of saturate gasoline on 2 meters "C" packing at 75°C. Helium at 10 psig. Sample size 0.01 ml.

Table I shows the operating conditions for this test. A Perkin-Elmer Model 154B Vapor Fractometer was employed. Any other type of gas chromatographic unit using the same column and operating procedure would be satisfactory. The column consisted of a two meter length of ¼″ OD tubing packed with 35 wt. % of silicone fluid on Celite 545 (Perkin-Elmer "C" packing). The column was operated at 75°C. with helium at 10 lb psig, a flow rate of 75 ml per minute, and a chart speed of 30″ per hour. Sample charge (both standard blend and sample) was 0.0100 ml. For accurately charging this volume, either the Gilmont micro syringe modified to take a standard luer hypodermic needle, or the micro pipette inlet system marketed by several instrument manufacturers is satisfactory.

Table II shows the composition of a synthetic blend prepared for us by Phillips Petroleum Company. This blend contains C_2 through C_5 saturate hydrocarbons in approximately the amounts in which they are present in a sample of hydroformate gasoline. The balance of the material is a 250 to 300°F. virgin naphtha fraction. When using the standard blend, both the standard and the sample should be cooled to ice water temperature prior to charging.

Figure 2 shows a recording of a chromatogram obtained on a saturate naphtha. After the elution of normal pentane, the column was back flushed to elute the C_6 and heavier materials. Back flushing is carried out for about 1.5 times the forward development time to insure complete removal of the heavy ends.

Table III lists the retention values (measured from air peak to hydrocarbon peak) and some peak height measurements obtained by us. Retention values are normally measured in millimeters. For convenience, this data is also given in seconds of elapsed time. Peak height values are ex-

TABLE III

CALIBRATION DATA

Hydrocarbon	Retention Time mm Past Air @ 30″/Hr Chart Speed	Seconds	Peak Height (mm) for 1% Conc. in 0.0100 ml
Ethane	4	19	300
Propane	6	228	257
Isobutane	9	43	215
n-Butane	12	57	199
Isopentane	23	109	125
n-Pentane	28	132	117

$$\text{Vol.\% HC} = \frac{\text{HC Peak Height (mm)}}{\text{Std. Peak Height}} \qquad \text{Wt.\%} = \text{Vol.\%} \times \frac{\text{Density Pure HC}}{\text{Density Sample}}$$

pressed as millimeters of peak height for one volume per cent of a given hydrocarbon on a 0.0100 ml charge. Calculation of light ends is obtained from peak height, where concentration (volume %) in the sample is directly proportionate to peak height. Density values are used to convert to weight per cent, if desired.

Accuracy is equal to ±2% of the amount of the compound present (at 95% confidence level). Repeatability is within ±1% of the amount present. Accuracy of this method is equal to or better than that obtained by conventional methods. It has the added advantage of making it possible to analyze directly for light components in the presence of heavier components. Total running time plus calculation should not exceed twenty-five minutes per sample.

DISCUSSION

WINTERS (*Standard Oil Company, Indiana*): You determined your calibration factor at one concentration. Do you use that for all concentrations or all peak sizes?

DIETZ: Yes, we do. In general our ranges will run about that shown here, but they can vary as much as three- to fivefold over these values.

WINTERS: But you use a single factor?

DIETZ: Yes. The curve is linear over that range.

Chaper X

The Analysis of High Vapor Pressure Natural Gasolines

R. A. Meyer

Consolidated Electrodynamics Corp., Pasadena, California

Sampling and analysis of volatile liquids contained in high pressure sample bombs has long been a serious analytical problem. I will discuss how a new chromatograph has simplified this type of analysis to the point where it no longer requires a high degree of operator skill. This new instrument provides both the sample vaporizer for truly quantitative sampling and a pre-cut column for disposing of unwanted heavies while analyzing the desired light ends. It is of modular construction. Where the application requires the use of more than one column, or columns at different temperatures, two or more analyzer units may be used with one control unit. Each analyzer is, of course, a separate unit, containing in a thermostated oven its own valve, columns, and detectors. Thus the analyst can have two or more completely independent sets of chromatographic parameters available for immediate use. If only a single set of parameters is needed, a single analyzer and control unit form a complete chromatograph.

Let us first consider the problem of transferring a representative sample of the liquid into the chromatograph. We should have a typical sample to discuss so let's choose an 88 pound vapor pressure natural gasoline. The Podbielniak analysis of this mixture is shown in Fig. 1. It is present as a liquid under 88 pounds per square inch pressure in a sample bomb. If one were to attempt sampling by normal chromatographic techniques, such as with a hypodermic syringe or by capillary introduction, all the instrument would measure would be the heavy ends. Similarly, a gas sample would in no way be representative of the liquid composition. Figure 2 shows the new method of sample introduction from a high pressure bomb. It is as simple as connecting a capillary tube to the liquid outlet of the sample bomb, allowing a short flow stabilization time, and rotating the knob a few degrees. The valve in use in the photograph is connected to an internal tube leading to the bottom of the bomb.

The sample, taken from the liquid phase in the high pressure bomb, is passed through a flow reduction capillary, into a flash vaporizer chamber, and through the heated sample valve as a gas, where it purges the sample loop and exhausts from a port in the front of the oven. When the sample loop has been purged with the material to be analyzed, a knob on the oven panel is rotated a few degrees. This action detaches the sample loop from the sample purge line and places it in the flowing carrier gas stream. It is

Methane	0.3%
Carbon Dioxide	0.1
Ethane	3.5
Propane	29.0
Iso Butane	8.0
Normal Butane	20.0
Pentanes and Heavier	39.0

FIG. 1. Distillation analysis of 88 pound natural gasoline.

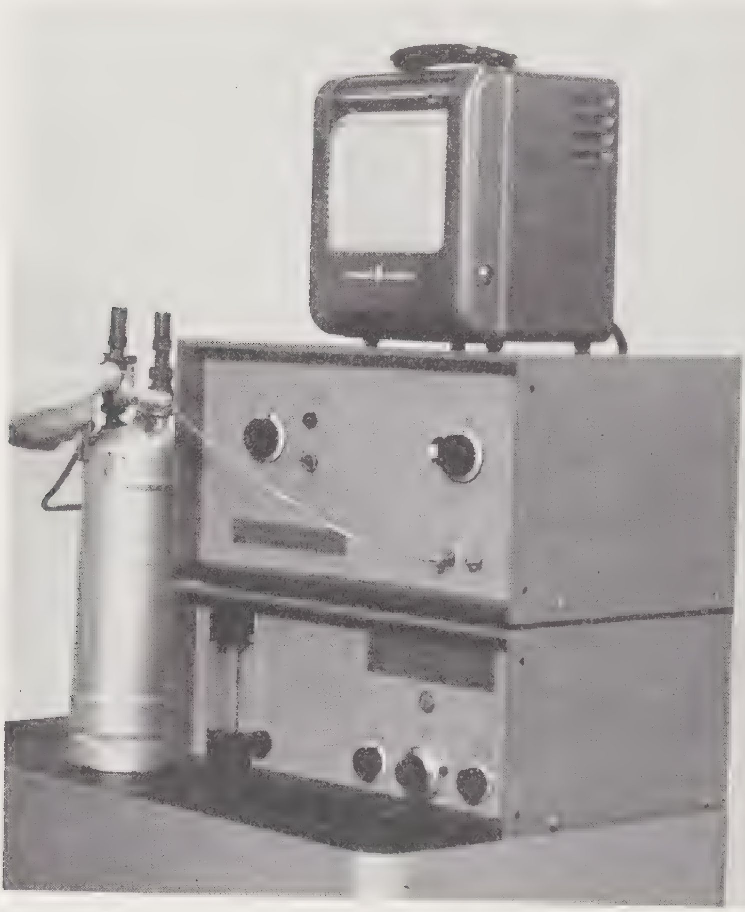

FIG. 2. Sample introduction method for high vapor pressure liquids.

then swept into the first of the two columns. The valve is located within the thermostated oven chamber to preclude condensation of heavy ends within the sample loop and insure the admission of highly reproducible sample volumes, as shown by Fig. 3. Here we see repeat analyses, not of the ideal single component samples, but rather of a complex, wide boiling range, high vapor pressure gasoline. The figure shows the ethane through pentane portions from three runs on the 88 pound natural gasoline chosen as an example. For ease of presentation, all peak heights have been reduced by a factor of 30. Had the various positions of the stepwise attenuator been used, the methane peak would have been visible.

It is worthy of comment that the separations are, of course, dependent upon operating conditions. The chromatograms shown were made with a ¼-inch diameter, 21-foot long column packed with 25% Eicosane on C-22 firebrick. The oven temperature was 130°C and the helium flow rate 35 cc/min. Other columns or conditions could have been chosen to yield different resolutions.

Figure 4 shows the valve in more detail. The ten port design permits five switching operations to be made with a single movement of the operating knob. The tungsten carbide lower face mating with the stainless steel upper

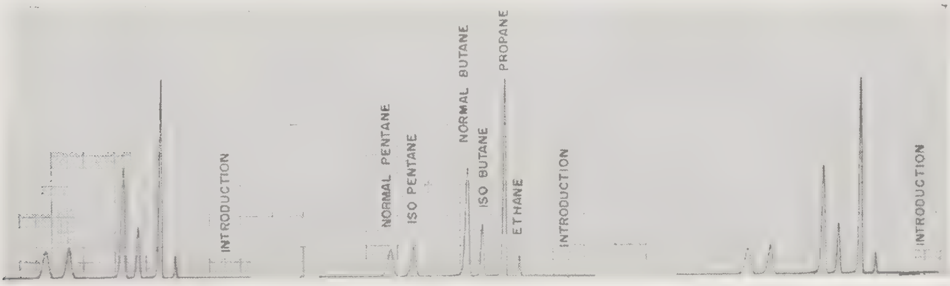

FIG. 3. Repeat analysis of 88 psi natural gasoline. All peaks ×30 attenuation. Column 21 feet long, ¼ inch diameter filled with 25% Eicosane on C-22 firebrick. Oven temperature 130°C. Carrier gas helium at 35 cc/minute.

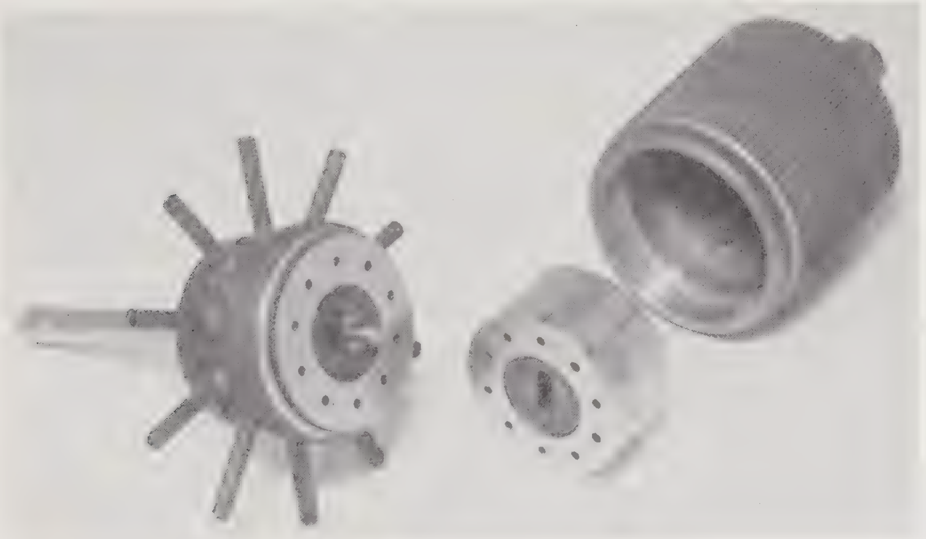

FIG. 4. Ten-port valve.

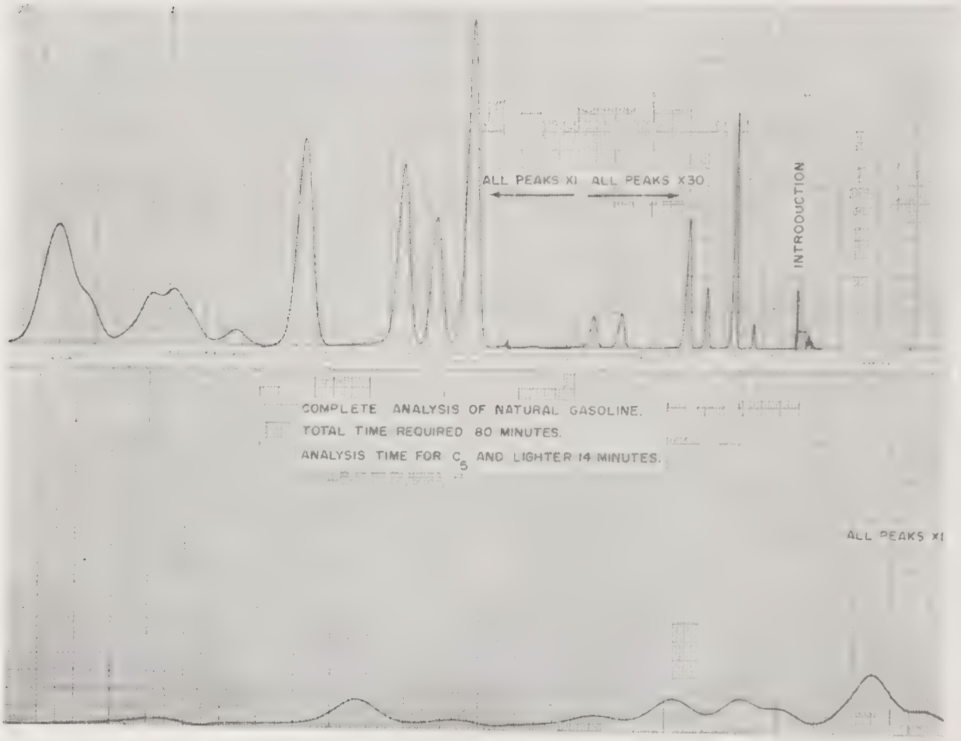

FIG. 5. Complete analysis of natural gasoline.

face insures long valve life. The outside of the valve is enclosed within a chamber pressured with carrier gas at column head pressure. This greatly extends the period between greasings and reduces the possibility of leakage. All units are leak checked with a helium leak detector.

Now that a precisely measured sample has been admitted to the chromatograph, let us see how it is analyzed. Figure 5 presents a chromatogram showing the complete analysis of the natural gasoline sample. As you can see, it would be a time consuming procedure to wait 80 minutes for the 18 partly resolved fractions to appear, especially when the unit operator is only interested in the C_5 and lighter portion of the sample. Through the use of a pre-cut column, it is possible to divide the sample between the normal pentane and lighter portion, and the hexane and heavier fraction. This reduces analysis time to only 12 minutes. While analysis of the low boiling portion of the sample is carried out in the normal manner, the pre-cut column is back flushed to eliminate the unwanted heavy fraction. This is accomplished by rotation of the valve knob back to the sample purging position. It is then possible to attach a fresh sample. Thus the three functions of (1) sample analysis, (2) back flushing to discard the unwanted fraction, and (3) purging of the sample volume with a new sample can proceed simultaneously. At the conclusion of one run, the appara-

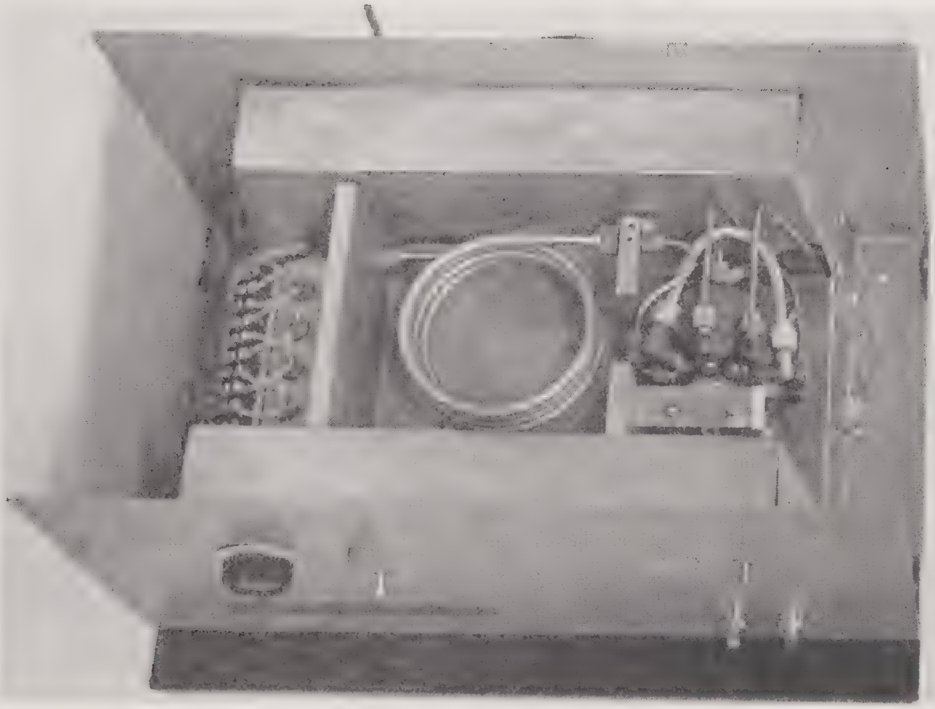

FIG. 6. Analyzer unit, interior view.

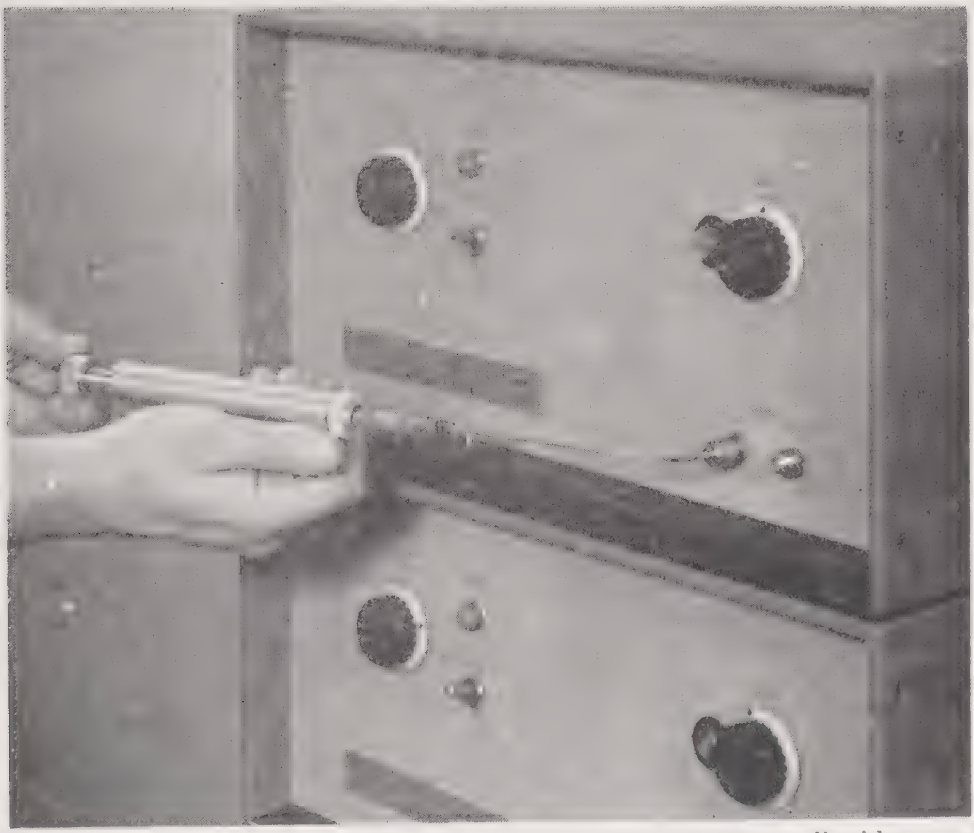

FIG. 7. Sample introduction method for low vapor pressure liquids.

tus is immediately ready to start another. In the analysis shown, this feature allows the operator to make over five runs during the time required for a single one if he did not have the pre-cut column in his apparatus.

Figure 6 shows the inside of the analyzer module. From bottom to top are the detector block, main column, and sample valve with its attached pre-cut column and sample loop. The sample vaporizer is buried within the fiberglass insulation. The oven is very well insulated. In fact, I have operated a standard unit at 380°C and still used the top of the analyzer as a writing table.

When the chromatograph is used for routine analysis it has been found that a simple calibration on a peak height basis suffices. We recommend calibration with blends whose composition brackets the normal spread of the samples to be analyzed. Another very satisfactory method consists of continuing with the method of analysis in use before installation of the chromatograph. The samples are run by both methods for a short period of time and percentages as determined by the previous method are plotted against peak height. This calibration can be obtained at little cost. When using peak height calibration, it is advisable to retain a standard sample checking column conditions and possible adjustment of the calibration curve.

The instrument comes equipped with a device for the admission of liquids which are stable at room temperature (Fig. 7). It consists of a screw-driven hypodermic syringe which acts as a pump to force the liquid through a short capillary and into the vaporizer. Thus it is possible to sample liquids with the previously demonstrated high precision.

In conclusion, a new technique of chromatography, that of direct sampling from high pressure liquid sample bombs, has been opened up through the efforts of an instrument manufacturer. High vapor pressure liquid analyses can now be considered just another routine task for the laboratory chromatograph.

CHAPTER XI

Quality Control of Chlorofluoromethanes And Chlorofluoroethanes by Gas Chromatography

M. J. ROOT

G. Barr & Co., Chicago, Illinois

The chlorofluoromethanes and chlorofluoroethanes, which originally were developed for refrigerants, have now found an extended use as propellents in "pressurized packages" referred to as "aerosols." Those commonly used in this industry include:

		B.P. °F.
Type 11	CCl_3F	74.7
Type 114	$CClF_2$-$CClF_2$	38.4
Type 101	CH_3CClF_2	15.4
Type 100	CH_3CHF_2	−13.0
Type 12	CCl_2F_2	−21.6
Type 22	$CHClF_2$	−41.4

These materials have boiling points that range from about room temperature to 40 below zero. Derivatives of these compounds can range from methane and ethane to the various chloro-fluoro compounds and finally to the completely fluorinated compounds.

It has been shown by Percival (*1*) and Root and Maury (*2*) that gas chromatography can be applied in the analysis of these compounds, whose trade names are Freons, Genetrons, and Isotrons. Janak (*3*) reported on the separation of a number of fluorinated hydrocarbons.

The first chromatogram (Fig. 1) shows a separation of the following:

			B.P. °F.
Freon 11	Trichlorofluoromethane	CCl_3F	74.7
Genetron 101	Difluorochloroethane	CH_3CClF_2	15.4
Genetron 100	Ethylene Fluoride	CH_3CHF_2	−13.0
Freon 12	Dichlorodifluoromethane	CCl_2F_2	−21.6

Separation of these four compounds is readily accomplished under the conditions given. Vapor pressure and specific gravity have been used for analysis of the chlorofluoromethanes and ethanes, but such methods are not positive identification. Thus, a mixture of carbon tetrachloride and dichlorodifluoromethane could give identical measurements of vapor pres-

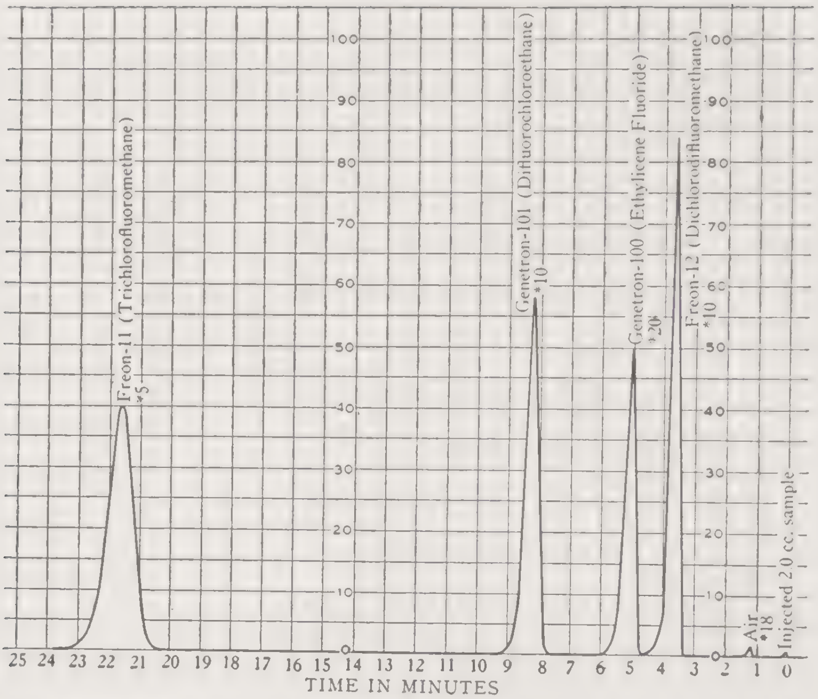

FIG. 1. Chromatogram. Separation of trichlorofluoromethane (Freon® 11), difluorochloroethane (Genetron® 101), ethylene fluoride (Genetron® 100), and dichlorodifluoromethane (Freon® 12).

sure and specific gravity with a mixture of trichlorofluoromethane and dichlorodifluoromethane. Such physical measurements are only useful when the identity of the components is known. Mass spectrometry and infrared spectrophotometry have also been used for analysis of mixtures of these types of compounds, but quantitative relationships are not as easily and readily obtained as with gas chromatography.

Table I shows the analysis of mixtures of trichlorofluoromethane and dichlorodifluoromethane by four different methods, density, pressure,

TABLE I

ANALYSIS OF MIXTURES OF TRICHLOROMONOFLUOROMETHANE (F-11) AND DICHLORODIFLUOROMETHANE (F-12) BY VARIOUS ANALYTICAL PROCEDURES

	F-11/F-12	F-11/F-12	F-11/F-12
Nominal	35 /65	50 /50	60 /40
By density	34.2/65.8	49.4/50.6	60.0/40.0
By pressure	34.0/66.0	50.5/49.5	60.1/39.9
By infrared	33.5/66.5	49.0/51.0	60.1/39.9
By chromatography	34.0/66.0	49.9/50.1	60.5/39.5

infrared, and gas chromatography. All methods agree very closely and it would be difficult to determine which is the most accurate. With the gas chromatographic method, given a specific standard sample, the accuracy of analysis would depend only upon the repeatability of the instrument.

Figure 2 shows the analysis of a mixture of equal parts of trichlorofluoromethane and dichlorodifluoromethane containing 1% carbon tetrachloride. Very good separation is obtained on a six-foot hexadecane column although the boiling point range is from 170°F. (CCl_4) to -21.6°F. (CCl_2F_2). The 1% carbon tetrachloride is readily detectable in this mixture at highest sensitivity.

The next chromatogram (Fig. 3) is also a mixture of equal parts Freon 12 and Freon 11 to which was added 1% 1,1,1-trichlorethane. Here again the sensitivity was at a maximum for the trichlorethane and the sensitivity for the other components was $\frac{1}{50}$th as great. There would be no difficulty in detecting a fraction of one per cent of 1,1,1-trichlorethane in the mixture of trichlorofluoromethane and dichlorodifluoromethane.

Figure 4 is a chromatogram of a similar mixture of equal parts of Freon 11 and Freon 12 with 1% of chloroform added. Here again 1% of this chlorinated hydrocarbon is readily detected in this mixture of chlorofluoromethanes. The sensitivity of the first two peaks was set at 20, whereas the sensitivity for the chloroform peak was at maximum.

A more defined peak and a faster elution time can be obtained by shortening the column length. Figure 5 shows the same analysis as is shown in Fig. 4 except that the column was shortened to 18 inches. Where the elution time is too long and the peak becomes poorly defined, it is possible to shorten the column and obtain faster elution and a better defined curve.

As has been shown by Browning and Watts (*4*), and Root and Maury, in solutions in which the difference in thermal conductivities of the components is small, areas under the curves obtained may be used to determine

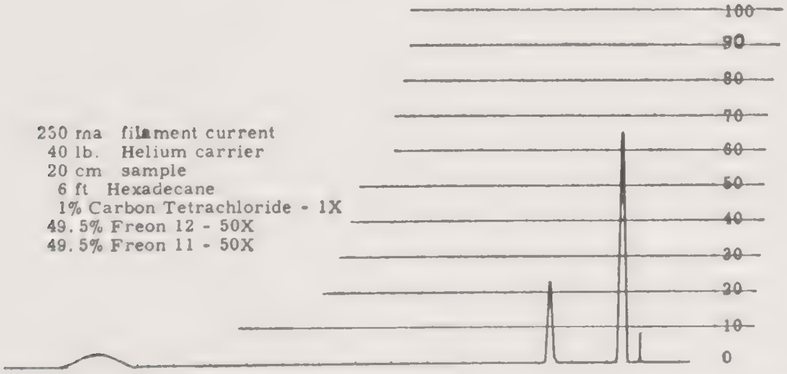

FIG. 2. Chromatogram. Detection of 1% carbon tetrachloride in mixture of equal parts trichlorofluoromethane (Freon® 11) and dichlorodifluoromethane (Freon® 12).

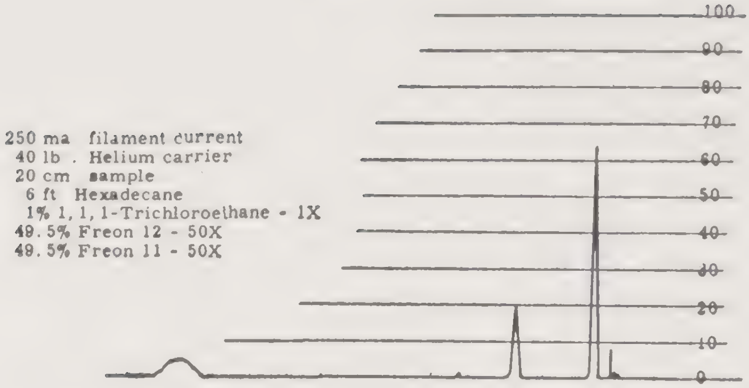

FIG. 3. Chromatogram. Detection of 1% 1,1,1-trichlorethane in mixture of equal parts of trichlorofluoromethane (Freon® 11) and dichlorodifluoromethane (Freon® 12).

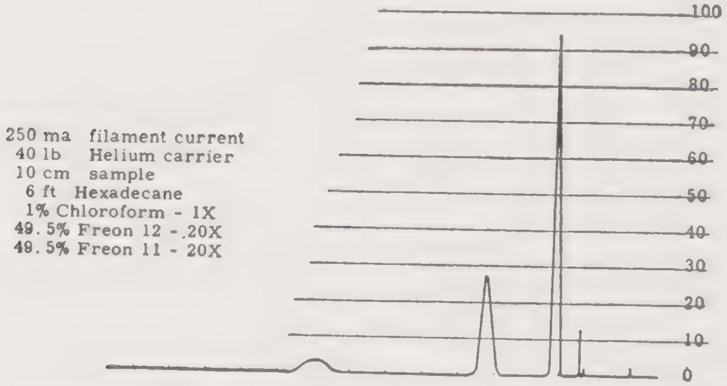

FIG. 4. Chromatogram. Detection of 1% chloroform in mixture of equal parts trichlorofluoromethane (Freon® 11) and dichlorodifluoromethane (Freon® 12).

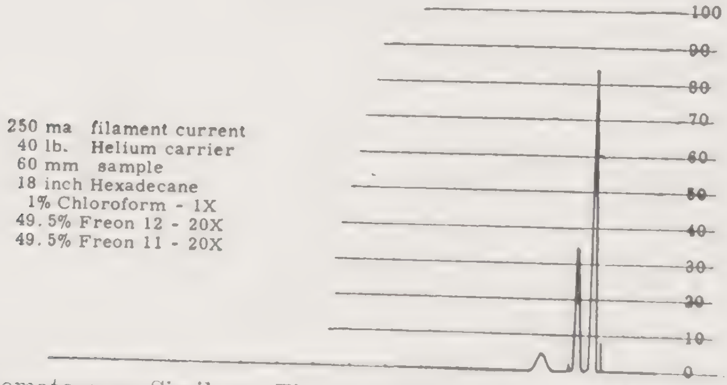

FIG. 5. Chromatogram. Similar to Fig. 4 with column shortened to eighteen inches.

weight per cent directly; however, where thermal conductivities differ, division of the individual areas by the thermal conductivities of the compounds allows calculation of the weight per cent. The thermal conductivities of the chlorofluoromethanes and ethanes studied are sufficiently close to make such a correction unnecessary.

Since gas chromatography not only furnishes a quantitative analysis but also positively identifies mixtures of chlorofluoromethanes and ethanes, it is a useful tool for the quality control of such chemicals. These materials are used in tank car quantities by "aerosol" manufacturers. It frequently is necessary to sample and analyze such tank cars prior to pumping into storage tanks. The use of gas chromatography has made it possible to sample tank car mixtures of propellent by means of a "thief" and determine in about fifteen minutes the composition and identity of the mixture. This could not previously be accomplished by any of the other analytical techniques.

Acknowledgment

Acknowledgment is made to Mr. M. J. Maury and Mr. H. Musleh for their assistance in obtaining the data reported.

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2. Root, M. J., and Maury, M. J., *Proc. 43rd Annual Meeting Chem. Specialties Manufacturers Assoc.* Washington, D. C. December, 1956.
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DISCUSSION

CAFLISCH (*Union Carbide Olefins Co., West Virginia*): Have you had any experience in trying to separate Freon-114 from its isomer by gas chromatography, or the other Freons that do have isomers?

ROOT: Yes, we did some work with Freon-114 and its isomer, Genetron-320, but have not been successful in separating these two isomers.

ANONYMOUS: How do you operate a high pressure thief from a tank car?

ROOT: The thief, which is a high pressure tank, is equipped with valves at each end. The thief is connected up to the tank car so that the liquid phase enters into the thief. The other valve is held at the top in an open position. As soon as the thief is liquid full, the lower valve is closed, but the upper valve is left open to allow some of the propellent to be poured off. The valve is then closed and the thief contains an air-free sample of propellent.

CHAPTER XII

The Use of Gas Chromatography in Kinetic Studies

LEWIS F. HATCH

Department of Chemistry, The University of Texas, Austin, Texas

Gas chromatography is being used at the University of Texas in kinetic studies on such widely divergent reactions as the thermal decomposition of acetylene between 600° and 900°C, and of butane between 560° and 600°C, and the isomerization of the 1-bromo-1-propenes by ultraviolet light at 40°C. The same basic chromatographic equipment is being used for all of these studies and consists essentially of a Gow-Mac thermal conductivity cell as the detector and an adjustable-range Brown Recorder. The adsorption columns were fabricated from $\frac{1}{4}$-inch copper tubing and were immersed in an oil bath containing a special heat resistant oil (Shell Tellus 41 lubricating oil) furnished by the Shell Oil Company. The rest of the accessories were conventional. The equipment was assembled at a total cost of about $1300.00 with the major cost being the recorder.

A variety of columns was tested, using carbon, Linde Molecular Sieve, Curtin X_3 Universal Adsorbent, and other materials as packing. The two most useful are a 9-foot activated carbon column for light hydrocarbons and a 10-foot column with the Curtin X_3 Universal Adsorbent for benzene and other aromatic hydrocarbons. A 13-foot column is used for the analysis of the 1-bromo-1-propenes. A 30-foot column is used for hydrogen with nitrogen as the carrier gas.

The purpose of the decomposition studies on acetylene and butane is to obtain specific reaction rate constants, reaction orders and apparent activation energies from a flow system.

The gas chromatographic analysis of products of the acetylene decomposition showed, as was to be expected, primarily hydrogen, benzene, and ethylene, with small amounts of styrene—a difficult mixture to analyze readily and inexpensively except by gas chromatography. No satisfactory method has yet been found for a simple, direct comparison of the hydrogen produced by decomposition with polymer formation in this reaction; but comparative studies in duplicate experiments with measurements of pressure effects and analysis using 9-foot and 30-foot carbon columns have given positive results.

Data were obtained in a flow system for butane decomposition at 560°, 580°, and 600° using specific calibration data for the chromatographic analysis of the products. The compounds involved in the kinetic study were: methane, ethane, ethene, propene, and unreacted butane. Figure 1 illustrates the precision of the data obtained with ethene as the gas measured. These data are not typical but they are actually the best we have obtained. Figure 2 shows the other extreme of precision. An activation energy for the decomposition of butane was obtained from the rate constants extrapolated to zero conversion.

The influence of additives on the decomposition of butane is also being studied. The value of gas chromatography in this type of investigation is illustrated in Fig. 3. The influence of small amounts of added propene is clearly shown by the general decrease in the amount of methane, ethane, and ethene produced and also in the change in ratio of the three compounds. Changes of this magnitude would be very difficult to obtain from a flow system as quickly by any other means.

Isomerization of the 1-bromo-1-propenes (Fig. 4) represents two problems which were solved by gas chromatography. The first problem was to obtain pure samples of each isomer. Their boiling points are too close to-

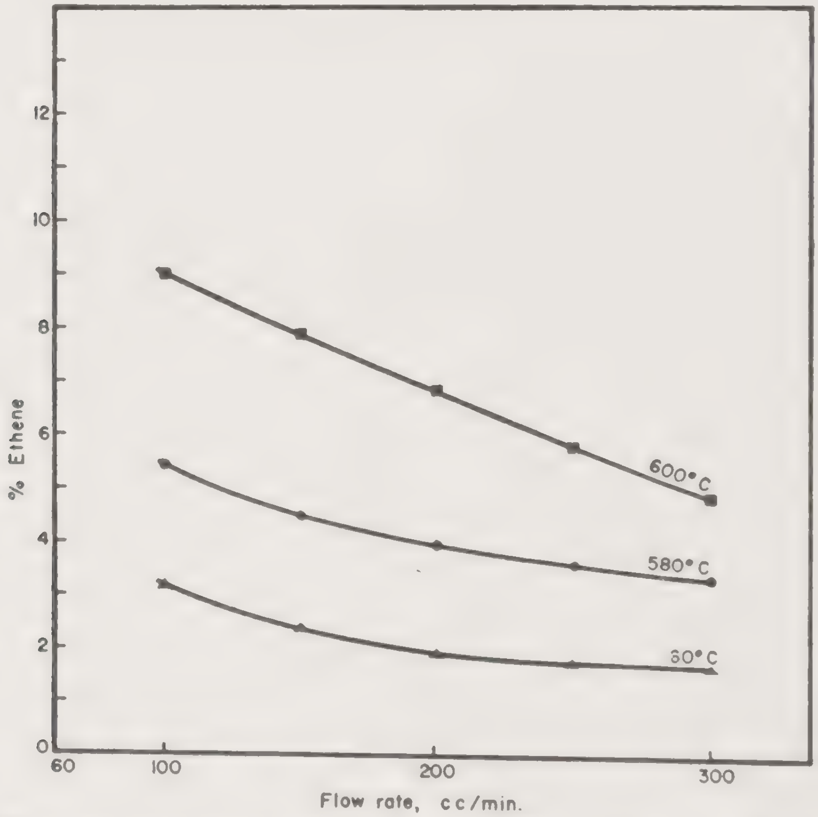

FIG. 1. Pyrolysis of a butane-helium mixture; 90% butane, 10% helium. Data representative of the best precision obtained.

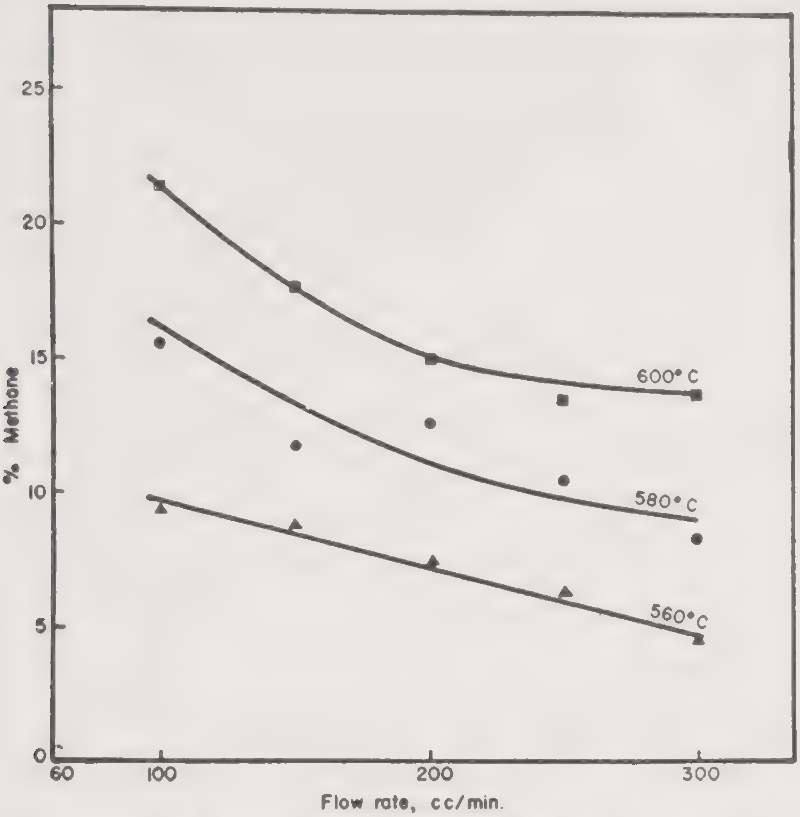

FIG. 2. Pyrolysis of a butane-helium mixture; 90% butane, 10% helium. Data representative of the poorest precision obtained.

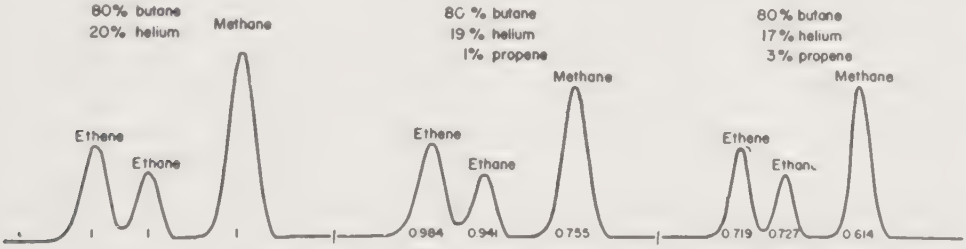

FIG. 3. Influence of additives on the pyrolysis of butane. Temperature = 580°C., flow rate = 100 cc/min.

gether and they isomerize too readily to permit clean separation by fractional distillation. The isomers are separable by gas chromatography. Pure samples of the two isomers were obtained by using a 20-foot, ½-inch copper column and Curtin X_3 Universal Adsorbent at 50°C. with helium as the carrier gas. The samples were frozen out with Dry-Ice.

The second problem was to analyze the isomerization mixtures. Infrared analysis was tried but was unsatisfactory because of the lack of a characteristic absorption which could be used for each isomer. The only two peaks available were too heavy for accurate analytical work. The use of gas chromatography with a 13-foot, ¼-inch column of Curtin X_3 Universal Adsorbent proved to be the answer. A synthetic mixture of the two isomers containing 24.5% (both weight and mole per cent) of the *trans* isomer analyzed as 24.3% *trans* which is an accuracy sufficient for kinetic studies. Figure 5 represents the precision of the data. From these data the rate of isomerization, the equilibrium constant and, by carrying

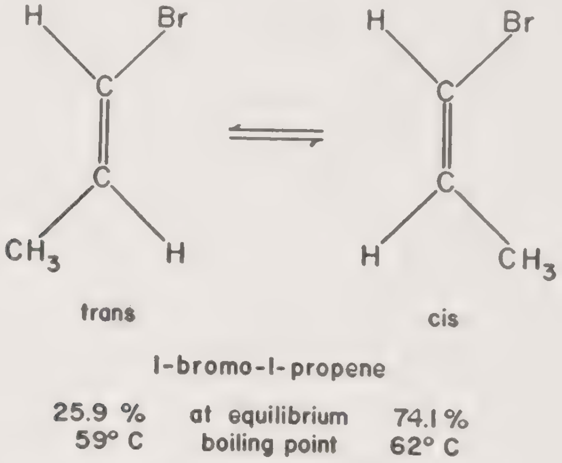

FIG. 4. The isomeric 1-bromo-1-propenes.

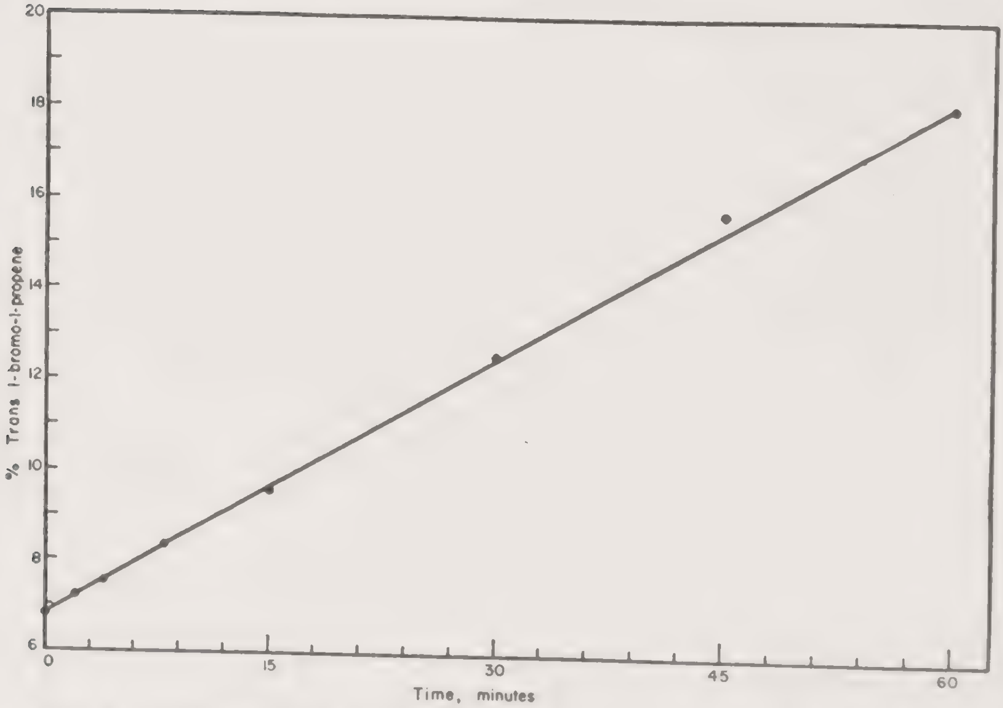

FIG. 5. Isomerization of *cis*-1-bromo-1-propene by ultraviolet light at 40°C.

out the isomerization at various temperatures, the activation energy can be determined. This information will be used to develop a theory as to the mechanism of the isomerization of the 1-bromo-1-propenes.

These examples of our use of gas chromatography have been presented to show the versatility of this technique in kinetic studies. More extensive data and conclusions will be presented in the literature when they have come to fruition.

Acknowledgment

The work on hydrocarbon decomposition is supported by the United States Air Force through the Combustion Kinetics Project, Contract AF 18(603)-142. The isomerization studies are supported by the Welch Foundation of Houston, Texas. This support is gratefully acknowledged.

DISCUSSION

ANONYMOUS: The pyrolysis technique you mentioned was not too clear. Would you care to elaborate on this?

HATCH: Actually, we were pyrolyzing in another tube, and taking samples out of the flow stream and putting them into our equipment. We expect to integrate a gas chromatographic set-up in our system so as to have a continuous, intermittent analytical system. Now we are simply sampling the product stream manually.

SANDLER (*Defence Research Board, Canada*): During the last five years, we have been studying the thermal decomposition of normal butane in a flow system at high temperatures and low residence times. It may be of interest to note that the apparent activation energy of the reaction under these conditions is decidedly different from that usually reported in the literature. This corresponds with the general statement you have made concerning the results of your studies in this field. We are preparing several papers on this work for publication and we shall be very interested in comparing our results with yours as they appear.

CHAPTER XIII

Some Applications of Gas Chromatography to Commonly Encountered Analytical Problems

J. L. MONKMAN

Department of National Health and Welfare, Occupational Health Division, Ottawa, Ontario, Canada

The Laboratory Service of the Occupational Health Division is concerned with unhygienic working conditions in industry and agriculture. In the course of evaluating working environments it becomes necessary to analyze such diverse samples as dry cleaning fluids, paint and lacquer thinners, degreasing solvents, solvent cements, and biological samples, among others.

Techniques and physical constants used for the organic liquid and gaseous samples in the past have included fractional distillation, boiling point, refractive index, molecular weight, density, and conventional gas analysis. When appropriate, organic derivatives were prepared and melting points determined. Analysis of a given solvent usually required at least two days, and more often a week was necessary.

After some years of experience with homemade vapor phase chromatographic equipment, the laboratory acquired a Perkin-Elmer Model 154 Fractometer. This instrument is now used routinely, and has cut down the time required for such analyses, as well as improving the accuracy. We would like therefore, in the following discussion, to bring to the attention of the overworked analyst some of our experience in this field.

The analytical technique used is conventional. Liquid samples are injected on the column using an Agla micrometer syringe. Gas samples may be injected with a hypodermic syringe or by using a gas sampling valve.

May we point out at the beginning, however, that we have not abandoned existing techniques, but have tried to assimilate the new technique as part of the total analytical armory. It must be realized that gas chromatography should not be expected to do things for which it may not be suitable. When a new analytical technique is introduced, there is a tendency to put all the analytical eggs in that basket, and to try to use it for all analyses. It is, of course, unwise to hastily drop established methods and instruments. A more cautious approach is usually justified, in which the new technique or instrument is introduced into the science in the light of all the accumulated knowledge of the past.

On the debit side, we must note that gas chromatography cannot directly handle substances of high solid content, or high viscosity. High boiling substances may be retained on the column, and there will be no evidence of their presence on the chart. The retention time, widely used as an index of identity, is not sufficiently specific, and is perhaps too readily influenced by the operating conditions.

On the credit side, we may say that the boiling point, refractive index, molecular weight, and density, of a distilled fraction are now completely definitive for identification of the fraction once the chromatogram has established that the fraction contains only one component (for example, as in Fig. 1, Fraction 5). This is an illustration of a new technique making older techniques more useful. The practical analytical applications of the mass spectrometer have increased enormously now that pure samples are more commonly available for analysis. Similarly, infrared identification has become practical and rapid since the analysis of mixtures is avoided. Before gas chromatography, it was a constant source of frustration to be told by the infrared expert, that the distillate fraction of current interest might contain some of A, B, C, and D but that it wasn't possible to say how much of each. This problem has been solved, as far as our laboratory is concerned, since we submit for infrared identification only fractions proven to be pure by chromatography (as in Fraction 5, Fig. 1). In fact, before the infrared results are available, we have a shrewd idea of the identity of the sample from the retention time, boiling point, and refractive index. With these four criteria you have an identification that cannot be shaken.

Some pitfalls, already hinted at, may be mentioned in some detail

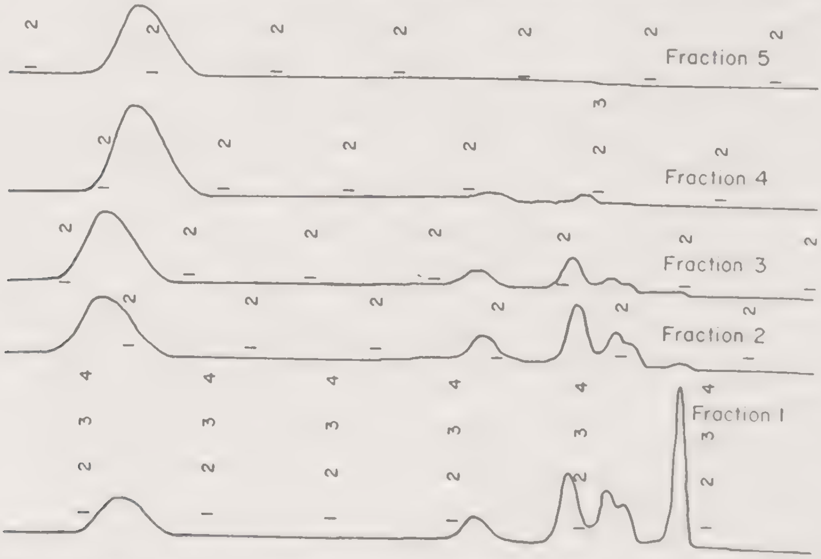

FIG. 1. Chromatograms of five separate distillate fractions of industrial cleaner.

The sensitivity of gas chromatography may be a disadvantage. The analyst, if new to the field, may be confused by the multitude of peaks found in an unknown sample. He would probably never have guessed at this complexity from a conventional gas analysis or distillation. At this point he must decide firmly whether it is necessary to identify and determine all the peaks found or not. It may be, and often is, quite sufficient to identify only one or two major constituents. If the beginner insists on identifying all components he may find that he has spent more time on the analysis than the sample deserves, and as much time as a conventional analysis would have taken before gas chromatography.

Gas chromatography is supplanting distillation as a laboratory technique, particularly in the natural gas and petroleum industries. This is only natural since the analysis is so quick and precise. It cannot, however, displace distillation completely. Samples which contain dissolved solids, or may be of a viscous nature are best handled by a preliminary distillation in a simple glass still, or a Dean-Stark apparatus, in order to separate the solid and liquid portions, after which the liquid portion may be analysed. Samples of this type encountered in our work include rubber and celluloid cements, naphthenate driers, and blood serum.

It may be found that one component of a mixed solvent cannot be eluted from the column if its boiling point is above the working temperature range of the particular instrument available. In this case the analyst may find only one component of a two component mixture and assume the sample to be a pure substance. This is an instance where distillation in a simple still, carried out at the same time as the chromatographic analysis, will readily show whether the material is a pure substance or a mixture.

By choosing an unsuitably low sensitivity setting a minor component may not appear. If the minor component is important, a gross error may be made. An illustration of this point is shown in Fig. 2 where an impurity appears in reagent grade benzene. This peak was not expected since the benzene was analytical grade, so it was not looked for. Quite by accident a run was made at the highest sensitivity and the unknown material showed up. It is wise, therefore, to make runs at several sensitivities, including the highest. Another consideration in this case, was the fact that to get a measurable peak for this unknown it sometimes was necessary, to concentrate the benzene by evaporation.

To summarize, in our laboratory gas chromatography is used:

1. To determine the purity of reagents and to follow the composition during purification procedures. See Fig. 3, which illustrates the purification of cyclohexane.

2. In place of, and together with, distillation procedures in the quantitative analysis of organic liquids.

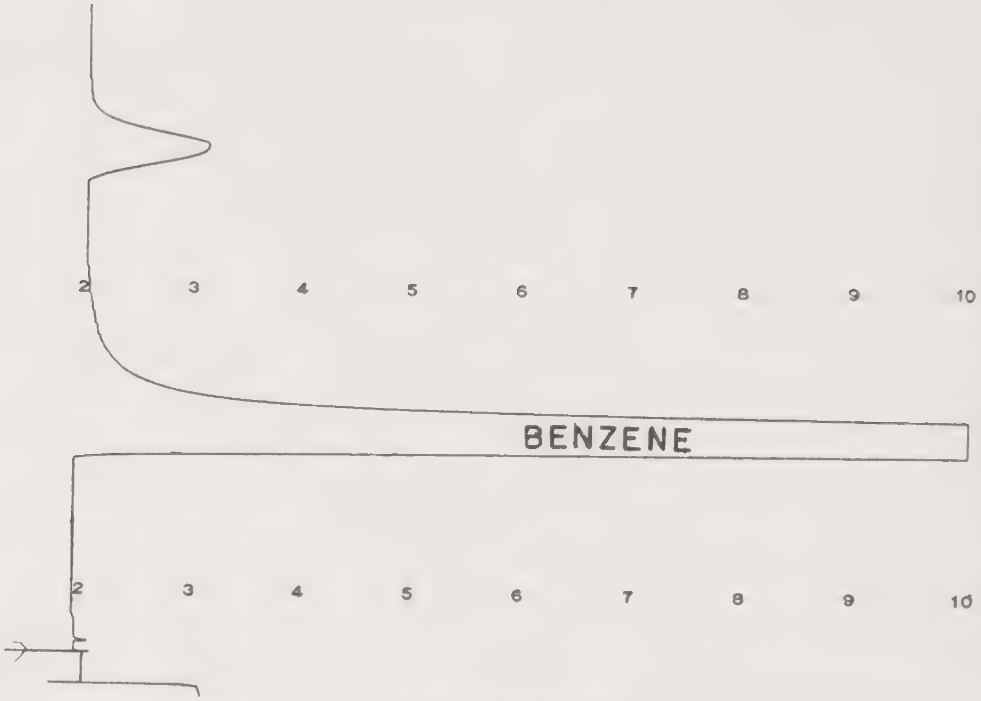

FIG. 2. Chromatogram showing impurity normally present in "reagent grade" benzene.

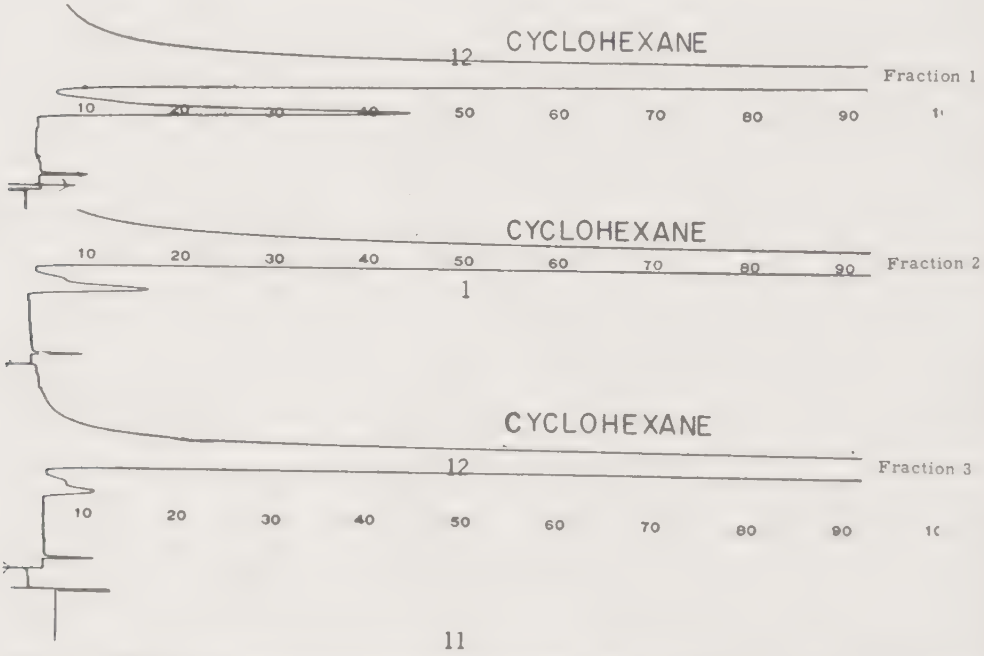

FIG. 3. Three chromatograms showing presence of impurity in cyclohexane before and during purification.

3. As the sole analytical technique, using retention times for identification, when no ambiguity is possible.

4. To assist in infrared and ultraviolet identification by preparing pure fractions for analysis.

5. To prepare pure substances either by the use of large preparative columns, or by repeated trapping of a smaller sample.

6. For the identification and determination of components by the application of conventional organic derivative techniques to the effluent gas.

Gas chromatography is a great comfort to the analyst because of its sensitivity, accuracy, and speed of analysis. The variable sensitivity control allows the analyst to avoid aliquoting. The permanent record cuts down laboratory bookkeeping, as it is only necessary to mark the chart before the run. When it does not supplant distillation it makes this procedure more meaningful and shows what reliance may be placed on refractive index, boiling point, and density. As instruments of higher sensitivity and higher temperative range are developed, the analyst's lot (if not the policeman's) may indeed become a happy one.

CHAPTER XIV

A Simple Electromechanical Integrator[a]

S. DAL NOGARE, C. EUGENE BENNETT, AND J. C. HARDEN

Polychemicals Department, E. I. du Pont de Nemours & Co., Inc.
Du Pont Experimental Station, Wilmington, Delaware

The usual quantitative interpretation of gas chromatograms is based on a correlation of peak height or peak area with concentration. Due to its simplicity, the peak height measurement is generally used where it is applicable. However, area measurements are frequently more reproducible and more linearly related to concentration. This is especially true for chromatographic peaks which have short retention times. The peak area measurement also finds wide use in analyzing unknown samples since in many instances the areas under the peaks can be related to sample composition with fair accuracy even without prior calibration.

This wide application of peak area measurements in gas chromatography necessitates a convenient means of measuring these areas. Area measurements in this laboratory have been made in various ways including planimetering, cutting out and weighing the paper under a peak, taking the product of peak height and width at half-height, counting squares under a peak, and the use of electromechanical integrators. Of these methods, certainly the electromechanical integrator is the most convenient and generally the most accurate.

Various commercial integrators, based upon mechanical, electromechanical, or electronic principles, can be purchased for between $400 and $900. The present paper describes a simple, electromechanical integrator costing about $150 for components and consisting of two gears, two Helipots, a stable low-cost d-c voltage supply, and a low-inertia d-c integrating motor.

APPARATUS

Three different low-inertia d-c motor-counter units manufactured by Electro Methods, Ltd., of Stevenage, Herts, England, designated Types 910, 913, and 918/3, and costing about $85 each, were evaluated in this work. Motors 913 and 918/3 were used interchangeably in one assembly while Motor 910 was evaluated in a slightly different assembly.

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[a] After this work was completed, the authors learned that similar work had been performed by Keulemans (*1*) and Desty (*2*). Unfortunately, only a brief description of the apparatus has been published (*1*).

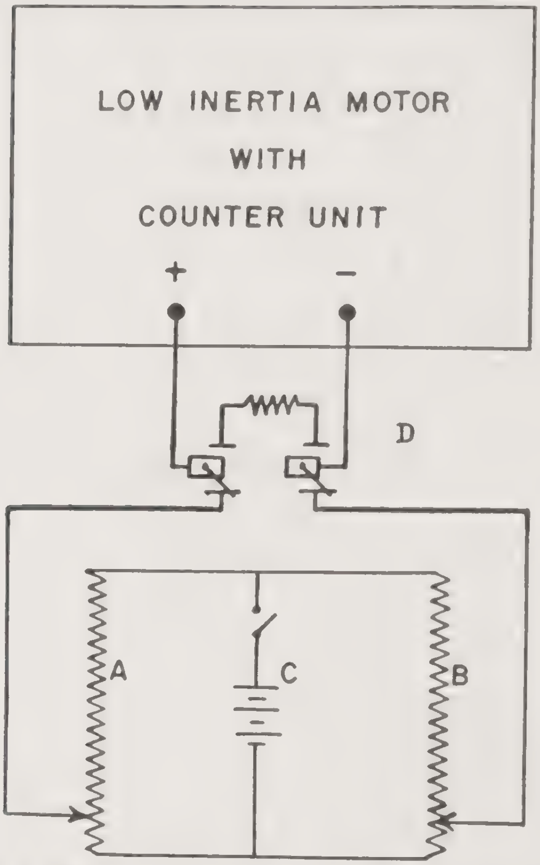

FIG. 1. Schematic drawing of integrator assembly.

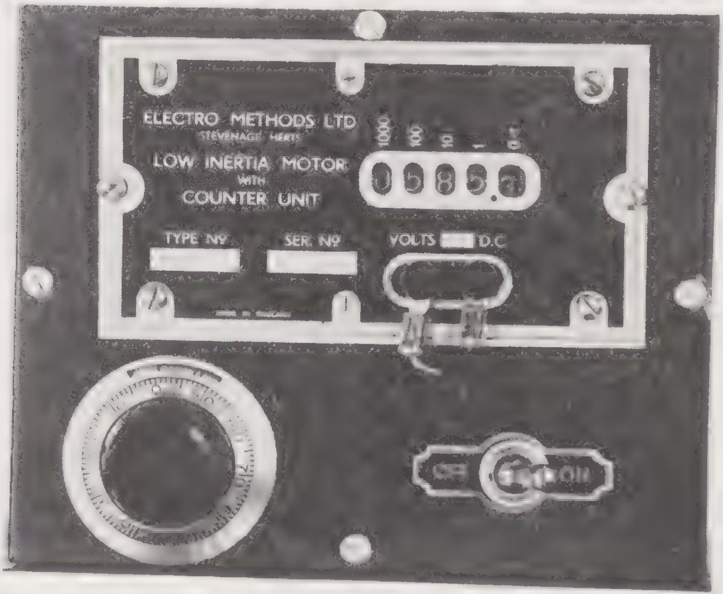

FIG. 2. Photographs of integrator (motor type 913) attached to recording po tentiometer (also the two photographs on the facing page.)

Principle and Operating Procedure

Essential features of the integrator are shown in Fig. 1. The heart of the apparatus is a low-inertia d-c motor-counter unit having a nearly linear counts-voltage relationship. Variable resistors are arranged in parallel with a suitable d-c power supply to form a bridge network. The variable contact in resistor A is mechanically coupled to the slide-wire shaft of a recording potentiometer. Thus, the voltage applied to the motor is a linear function of the pen position on the recorder. Variable resistor B serves as the zero control and is used to adjust the "zero" voltage to the motor at a value to

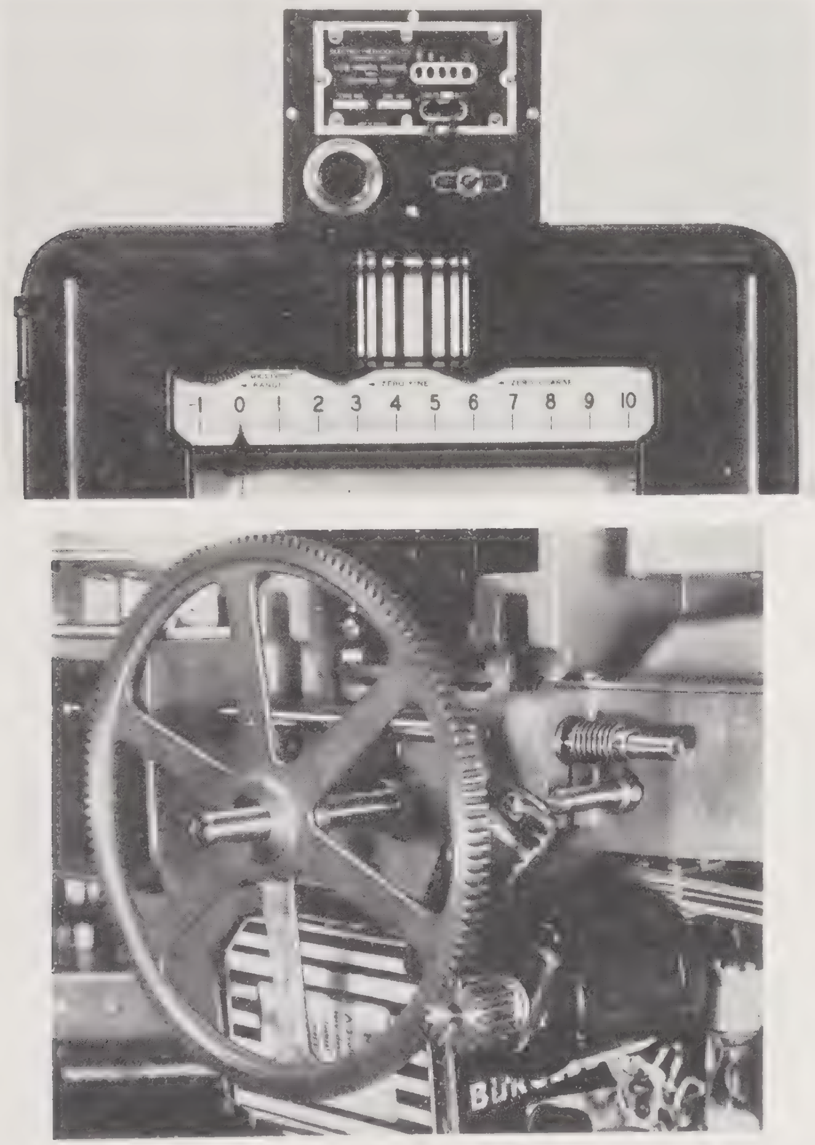

FIG. 2.—*Continued.*

prevent the counter turning but just sufficient to overcome the small start-up inertia in the device. In the data pertaining to counts-voltage relations, this small "zero" voltage was subtracted (Table III).

The operating procedure for the integrator consists of turning on the voltage to the bridge network by means of the switch C, adjusting the bridge voltage to the desired value, adjusting resistor B to the predetermined "zero" voltage while the recorder pen is at the baseline of the chromatogram, and recording the counter reading before and after each peak. The difference in the counter readings represents the area of the peak. If desired, a calibration factor can be used to convert this area to other units such as square centimeters, etc.

Instrumentation for Motor Types 913 and 918/3

Variable resistors A and B in Fig. 1 used with motor Types 913 and 918/3 were 1000-ohm, 10-turn Helipots (Series A) with ±0.5% linearity. The Type 913 integrating motor-counter, the bias Helipot, B, and the on-off switch were mounted in a steel box as shown in Fig. 2. The Type 918/3 motor is shown in Fig. 3. The variable contact in Helipot A was mechanically coupled (see Fig. 2) through a 9:1 gear train to the slide-wire drive of a Leeds and Northrup AZAR recording potentiometer having a chart range of −10 to 0 to +100 divisions. With the baseline at chart zero, full scale deflection of the pen supplied 75% of the applied bridge voltage to the motor. The data described in Tables I and II were obtained with 40 volts applied to the bridge and, therefore, full scale recorder deflection produced 30 volts at the motor. The reasons for selecting certain bridge voltages are given in the section of this paper describing the characteristics of low inertia d-c motors.

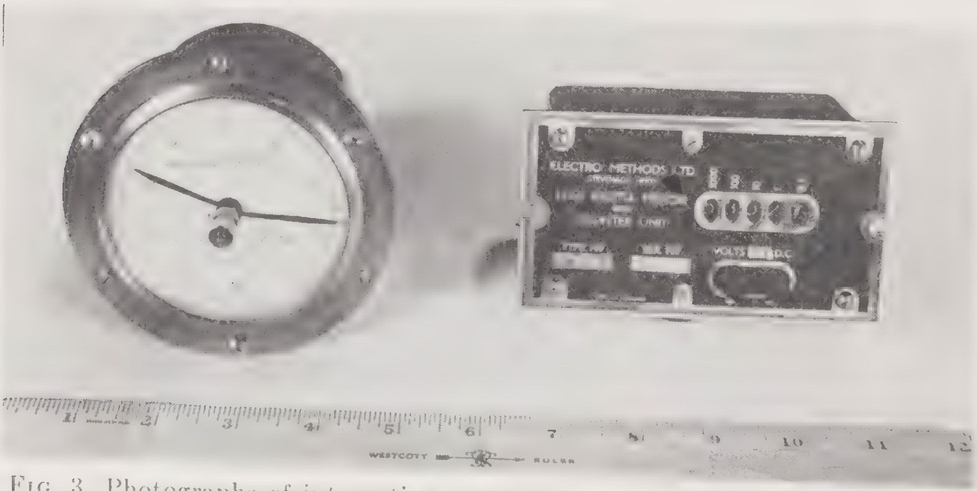

FIG. 3. Photographs of integrating motors type 918/3 prototype (left) and type 910 (right).

Two inexpensive power supplies were used in this work. One was a 30 volt d-c transistorized Transpac (Model TR 30, Electronic Research Associates, Inc., cost $65). Transpacs having other voltage ranges are also available. The other unit was a Heath Kit Variable Voltage regulated power supply (Heath Co., Benton Harbor, Michigan, cost $35.50 for kit) which supplies up to 500 volts.

At the start-up of an integration period, the bridge voltage was adjusted by means of the control in the power supply. In the case of the Transpac, the fixed voltage produced was used without adjustment. The applied voltage was accurately measured with a sensitive mv potentiometer (generally, a 1000:1 attenuation was used so the millivolt reading on the potentiometer corresponded to volts). The voltage need not be accurately reproduced for measuring peak area ratios in individual runs. If absolute area measurements are desired to compare data over extended periods of time, then accurate voltage settings are necessary.

The double pole-double throw switch, D, in Fig. 1 was connected so that the voltage to the motor could be turned off and the motor shunted simultaneously. A 5-ohm shunt caused the motor to come to a dead-stop. Severe coasting results if the shunt is not used.

The only modification required in the recorder was the exchange of one of the original electronic tubes (6L6) for the smaller but equivalent 5881. This was necessary in order to provide sufficient space inside the recorder for the gear train.

Instrumentation for Type 910 Motor

Variable resistors A and B in Fig. 1 used with motor Type 910 were 25-ohm, 10-turn Helipots (Series A) with ±0.1% linearity. The voltage applied to the bridge was 4 volts. This voltage was obtained directly from the 4-volt terminal of a lead storage battery or by reducing 6 volts to 4 volts by means of a 25-ohm variable resistor in series with the bridge. At maximum pen deflection on the recorder, 3.0 volts was produced at the motor. This value is two times the rated value of the motor. The other details of construction were the same as described for motors 913 and 918/3. The use of a 20- or 25-ohm transmitting slide wire available in both L and N or Brown recorders would eliminate the need for the Helipot and gear train when using the Type 910 motor.

PERFORMANCE OF INTEGRATORS

Practically identical results were obtained with each motor tested (Tables I, II, III, and Fig. 5). In general, the reproducibility of count rate at any given pen deflection was about 0.1 to 0.2%; the reproducibility of peak area measurements of gas chromatograms was about 0.3% for sharp peaks and better than 0.9% for broad peaks. The linearity of the integrators was about 0.3% over 3 to 100% of recorder scale. The maximum nonlinearity observed at 1% of recorder scale was about 2% relative. This error is minimized considerably for area measurements of moderate size peaks. For example, assuming a certain peak has a true area of 100 and that 10% of this peak falls in the maximum nonlinear range (2%) of the integrator, the integrated area would be 99.8 instead of 100 and the over-all error only 0.2%. An approximate average nonlinearity figure over the 0–3% range would be 0.6% relative. Therefore, in a hypothetical peak having an area of 100, and having 50% of its area in the 0–3% recorder range, the over-all error in area would be about 0.3%. Consequently, for practically all area measurements in gas chromatography, the accuracy of integration would be better than 1% and in most cases better than 0.5%.

Integrator Assembly Using Motor Types 913 and 918/3

Evaluation of the integrator using motor Type 913 was carried out by measuring the reproducibility of integration of air peaks, reproducibility of integration of a four-component mixture, and obtaining linearity checks on the gears, Helipots, etc., as well as on the counts-voltage curves of the motor.

The chromatogram of the three successive air peaks in Fig. 4 was obtained using the gas sampling valve of the Consolidated Type 26-201 Chromatograph. Attenuation of the detector output was used to vary the peak heights from 9 to 90% of full scale. The retention time of these peaks was about 30 seconds and the width at one-half peak height was about 1 mm. Peaks of this type are very difficult to integrate accurately by conventional means.

The reproducibility of integration for the air peaks (Table I-A) was calculated from the actual integrator counts. In reading the counter dial the count could be obtained to six digits (see Fig. 2) and the seventh digit estimated to ±0.5. A reading of 11.0 is in possible error of ±0.5 count. Thus, in the count data for the air peaks, the standard deviation for the smallest air peak is purely fortuitous.

The tabulation in Table I-B lists the per cent composition of a four component test mixture calculated from peak area ratios (ratio of peak count to total counts for the chromatogram in Fig. 4). The sample was introduced by means of an Agla micrometer syringe and the sample size was 20 μl. The standard deviation for all the peaks was in good agreement although the peak shapes and retention times varied widely.

The counts-voltage relationship for motors Type 913 and 918/3 is shown in Fig. 5. Motor Type 918/3 (prototype) was evaluated from −72 to −1 volts, and +1 to +50 volts. The linearity of both motors was about

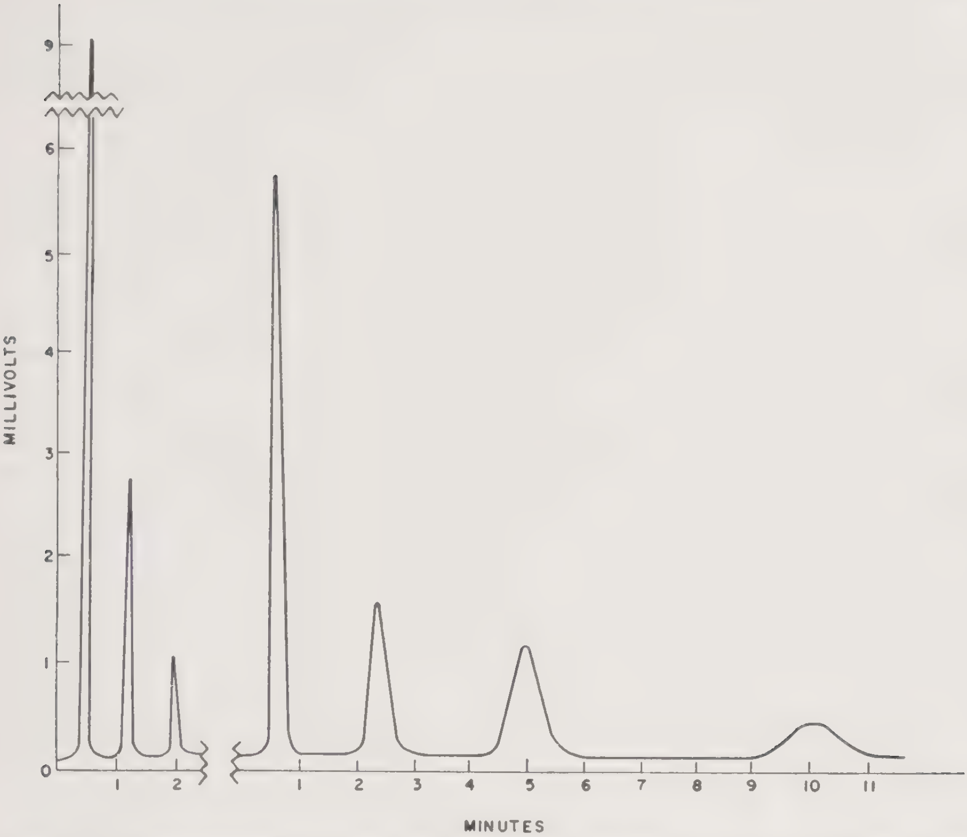

FIG. 4. Chromatogram of three successive air samples (left) and chromatogram of a mixture of methanol, *n*-hexane, trichloroethylene, and octene-1 (right).

TABLE I

DATA SHOWING THE REPRODUCIBILITY AND LINEARITY OF THE INTEGRATOR ASSEMBLY

A. *Reproducibility of Air Peaks*

No. of Runs	Integrator Average Counts	σ % Rel.[a]	Peak Description
6	106.3	0.47	1 mm × 90% scale
4	32.5	1.9	1 mm × 27% scale
3	11.0	(0)	1 mm × 9% scale

B. *Reproducibility of Four-Component Mixture*

Component	% by Area Ratio				
	1	2	3	4	σ, % Rel.[a]
Methanol	32.4	32.4	32.6	32.5	0.26
n-Hexane	20.4	20.3	20.3	20.4	0.25
Trichloroethylene	28.8	28.8	28.9	29.0	0.28
Octene-1	18.4	18.5	18.2	18.1	0.86

[a] σ, % Rel. = Coefficient of variation

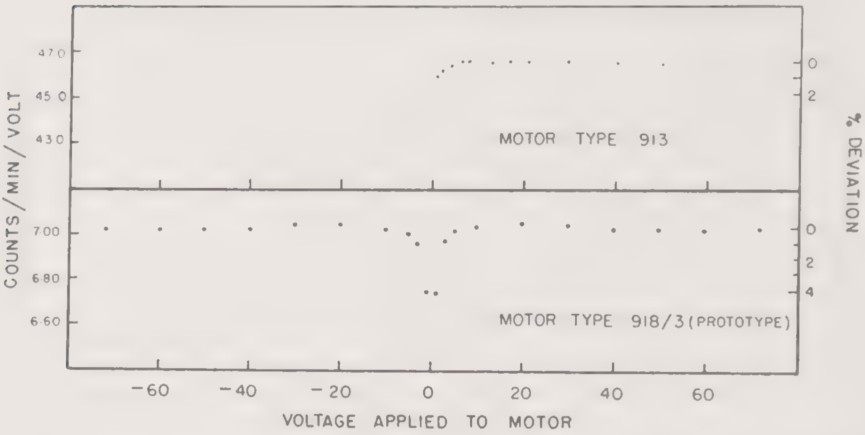

FIG. 5. Counts-voltage curves for integrating motors types 913 and 918/3 (prototype).

0.2 to 0.3% above 5 volts but was more nonlinear at lower voltages. For example, at one volt, motor Type 913 was about 1.3% from linearity while motor Type 918/3 was off by about 4%. This difference is reasonable since the Type 918/3 motor was a prototype. The linearity of these motors could be improved by adding a small voltage necessary to overcome the start-up inertia. Refer to discussion of results using Type 910 motor.

A final evaluation on the performance of the integrator was a check on the linearity of the gears and Helipots as well as the integrating motor, counter, and dial reading. The results are presented in Table II. Over the recorder range tested (5 to 90%) the linearity was better than 0.3%

TABLE II

LINEARITY OF INTEGRATING ASSEMBLY[a]

% of Recorder Scale	Average[b] Counts/min/div	% Deviation from Average
5	13.50	−0.3
10	13.51	−0.2
20	13.56	+0.1
40	13.55	+0.1
60	13.55	+0.1
80	13.56	+0.1
90	13.56	+0.1

[a] These data show the linearity of the motor, gears, Helipots, and recorder. The motor (Type 913) was used with 1000 ohm Helipots and 40 volts across the bridge. Refer to text for detailed discussion of linearity of motor.

[b] Obtained from duplicate 5 minute runs. Reproducibility of runs about 0.1% relative.

relative. The data were obtained by applying known potentials to the recorder (0.5 to 9 mv) from a calibrated potentiometer and determining counts per minute per chart division.

Integrator Assembly Using Motor Type 910

The data given in Table III show the linearity of the entire integrator assembly using motor Type 910 to be comparable to that obtained with motor Type 913 (Table II). The maximum nonlinearity observed at 1% of full scale was 1.6%. Above 3% on the recorder range the linearity was better than 0.5%. These results were obtained by applying the small "zero" voltage to the motor. Without the correcting voltage, the nonlinearity at 1% of full scale was 4.3%.

This low voltage motor (1.5 v) has certain advantages over the higher voltage Type 913 (24 v) in that the voltage source can be a simple storage battery. In fact, the same battery used to power thermal conductivity detectors can be used for the integrator. The low voltage also permits the use of a second recorder slide wire in place of the Helipot. This arrangement eliminates the need of a gear assembly.

TABLE III

LINEARITY OF INTEGRATOR ASSEMBLY AND SPEED-VOLTAGE DATA FOR MOTOR TYPE 910

% of Recorder Scale	Effective Voltage[a] Applied to Motor	Average Counts[b] min/div	% Deviation from Average	Average Counts[b] min/volt	% Deviation from Average
0	0.0012	0.0	—	0.0	—
1	0.0311	23.1	+1.8	743	−1.6
3	0.0898	22.52	−0.75	752	−0.40
5	0.1500	22.68	−0.04	756.0	+0.13
10	0.2987	22.62	−0.31	757.3	+0.30
20	0.5981	22.65	−0.13	757.4	+0.32
35	1.050	22.69	0.0	756.3	+0.12
40	1.200	22.75	+0.26	758.3	+0.44
60	1.810	22.72	+0.13	753.1	−0.25
80	2.413	22.66	−0.13	751.3	−0.49
99	2.987	22.72	+0.13	753.0	−0.26

[a] The effective voltage was obtained by subtracting the "zero" voltage from the applied voltage. The voltage listed for 0% of the recorder scale was the "zero" voltage. Other values were effective voltages.

[b] The values at 1% of recorder scale were not used in determining the average values. The count values were determined from long enough count times and total counts to give the significant figures indicated.

Characteristics of Low Inertia Integrating Motors

The low inertia motors used in the motor-counter units described in this paper are permanent magnet direct-current motors constructed to minimize friction, iron losses, and brush contact resistance. Since the motors operate from a few milliwatts power and have a fast time constant (Table IV), they can be used to integrate minute voltages on a time basis such as those obtained from thermocouples, photocells, ionization chambers (*3*), coulometric titrations (*4–7*), pressure transducers, etc.

The basic four types of motors (Types 900, 901, 902 and 903) made by Electro Methods, Ltd. (Table IV) are combined with a digital counter and marketed as Types 910, 911, 912, and 913. The designations become 915, 916, 917, and 918 with the radial counter. Various gear ratios are available

TABLE IV

Technical Data on Low-Inertia DC Motors

Motor Characteristics	Type 900	Type 901	Type 902	Type 903
Nominal voltage, v	1.5	6	12	24
No load starting voltage, mv	4.2	15	41	79
Increase for 1 g cm torque, mv	42	150	415	800
No load starting current, ma	1.5	0.375	0.18	0.095
Increase for 1 g cm torque, ma	15	3.75	1.88	0.95
No load current at nominal voltage, ma	15	0.9	0.45	0.225
Maximum-load current, ma	30	20	15	12
Starting current-full load, ma	535	150	54.5	28.5
Starting torque at nominal voltage, g cm	36	40	29	30
Starting power at nominal voltage, watts	0.8	0.9	0.65	0.686
Useful torque at nominal voltage, g cm	1.8	5.1	7.75	12.4
Useful load at nominal voltage, watts	0.035	0.097	0.117	0.145
Speed decrease for 1 g cm torque, rpm	55	50	69	66
Full load speed at nominal voltage, rpm	1885	1845	1405	1260
Ratio of speeds at starting and limiting voltages	1:1000	1:1000	1:1000	1:1000
Ratio of speeds at 1 g cm load	1:100	1:100	1:100	1:100
Armature resistance, ohms	2.8	40	190	700
Time-constant, m secs	10.5	9.4	12	12.3
Speed of motor, rpm	2000	2000	2000	2000
Moment of inertia of armature, g cm^2	1.8	1.8	1.8	1.8

although for gas chromatography applications, the fastest rate available is recommended. Thus, the Type 918/3 motor-counter (166 counts/min) which is six times slower than the Type 918 motor-counter (1000 counts/min) would not be recommended for integration of gas chromatograms. The radial counter can be read more easily and more accurately. For example, the radial counter can be read to 1000.0 ± 0.2 with ease while the digital counter can only be read to 1000.0 ± 0.5 with difficulty.

The speed of the motors increases about 2% when mounted in a steel box or placed near large amounts of magnetic materials. A slight improvement in the linearity of the motors also occurs. However, the manufacturer recommends that the motors be mounted at least four inches from other motors or magnetic materials. Apparently, this recommendation is made to eliminate changes in the motor characteristics from one location to another. As discussed previously, the motors become nonlinear at certain finite voltages. Consequently, operation at higher bridge voltages (Fig. 5) will result in more linear operation at the low recorder scale range. The manufacturer states that "the maximum voltage which can be applied to any of these motors is three times the nominal for limited duration." By operating the motor at two to three times the rated voltage for full scale recorder deflection, the counting rate and consequently the sensitivity of the integrator is increased by the same factor. However, it must be emphasized that the motors must not be operated at higher voltage ranges for long periods. For example, the Type 913 motor was damaged after twenty minutes of continuous operation at three times the nominal voltage. The voltage values generally used in this laboratory were twice the rated value of the motor but only in cases where the higher voltages were applied for short periods of time.

In addition to certain voltage requirements necessary to achieve optimum performance of the motor, certain current values are also required. For example, a marked improvement in the linearity of the Type 913 motor was achieved by using 1000 ohm Helipots instead of 5000 ohm values in the bridge circuit (Fig. 1). Similarly, Type 910 motor was completely unsatisfactory for integrating purposes using 1000 ohm variable resistors but gave good results using 25 ohm resistors. In general, more linear results would be expected (up to a limiting value) at any voltage range, the higher the available current. Thus the resistance values in the bridge network should be as low as possible. From a practical standpoint, the resistances used will be controlled by power rating of available variable resistors. For optimum performance, the actual power dissipation should be about half or less the power rating of the resistor.

The reproducibility of the motor at all voltages was found to be better than 0.2% relative. These values were found to be constant over a period of several months. There are certain conditions, however, that could cause variations. For example, the speed of the motor at no load varies about 0.35% per 10°C. Another possible source for error lies in the load on the motor produced by the counter. The digital type counter in Series 910/913 has an increased load as the second digit is turned, still more as more than one digit is turned simultaneously, etc. The radial type counter has constant loading and consequently eliminates this "erratic" loading.

Technical data on the motor-counter units comparable to the motors alone (Table IV) was not available at this writing. However, the manufacturers state that the starting voltage should not be more than 50% greater than no load values and the starting current about 10–15% over no load in the digital type counters. The radial counter is expected to require somewhat less starting voltage and current than the digital units. This increased load due to the counters could be eliminated by the use of a photocell arrangement or a miniature magnetic pick-up device on the shaft of the motor. These two techniques could then be connected to faster counters. The linearity of such devices should be even better than the motor-counter units as described in this paper.

Acknowledgment

The authors wish to express their appreciation to J. J. Bates, Jr., F. J. Debbrecht, and A. C. Webber for their helpful suggestions and assistance in the course of this work.

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Discussion

KNOBLAUCH (*Minneapolis-Honeywell Regulator Co., Pennsylvania*): Do you have any need for a pipping pen to use in conjunction with the integrator?

BENNETT: We have not used a pipping pen. I think this is due mainly to the fact that the early models we tried were not too satisfactory. It certainly would be nice if such a unit were available. At least it's nice in principle.

KNOBLAUCH: How rapidly would you like to have a pipping pen operate?

BENNETT: It is difficult to answer that question. We want the count rate as fast as possible. As I pointed out, with sharp peaks the count rate is very rapid and a small error of a slow counter would be very significant. If we can increase the count rate, the error would of course drop off. I would say that counting rates in the order of 2,000 to 5,000, or possibly 10,000, would be entirely satisfactory. That is counts per minute for full scale deflection.

KNOBLAUCH: 10,000 counts per minute? I am afraid that would be almost an impossibility.

SKARSTROM (*Esso Research and Engineering Co., New Jersey*): I am interested in learning if this motor heats up and changes its calibration. Does the motor have a temperature effect?

BENNETT: Yes, there is a temperature effect. Roughly 0.3 per cent per 10 degree change in temperature. We have not noticed, however, any change in the linearity pattern with operation.

SNOW (*Grace Research and Development Co., Maryland*): In reference to an earlier question, Brush Electronics has a pen which will handle 2400 counts per minute at full scale. This is about the limit, because it approaches the limit in readability.

BENNETT: I had assumed, when I made the suggestion of 10,000 counts, that we would have a pen that would be easy to read.

PINK (*Southwestern Industrial Electronics Co., Texas*): We have developed a readout device which provides a counter indication, enabling a precision of about 0.1 per cent to be obtained. It is entirely electronic, using a magnetic amplifier and transistors throughout. The device operates by amplifying the output of the chromatograph in the mag amp, the output of which is then fed into an analog-to-pulse-rate converter. This pulse rate is then compared to and subtracted from a "base line" pulse rate and the difference is scaled down by a factor of ten to operate mechanical counters. Two counters are obtainable, one to totalize the analysis, and the second to provide individual peak areas. It can also be used with a printer automatically. At the end of each peak a discriminator signals that a peak has been completed by turning on a light or printing out.

ANONYMOUS: What is the cost of this device?

PINK: This unit is not yet in full manufacture, but we feel that the price will be in the neighborhood of $1700.

BENNETT: I would like to ask Dr. Keulemans and Mr. Desty, who have a device similar to this of their own, if they would care to comment on its performance.

DESTY (*British Petroleum Co., Ltd., England*): We use a very similar set-up to that which you have described, but with a standard transmitting slide wire (200 ohm) on the recording instrument. In order to increase the count rate, we reversed the gear train between the motor and the counter. With regard to linearity, the main difficulty is the mechanical loading of the counter. Presently, we are working on a simple photoelectric arrangement to substitute for this mechanical linkage.

CHAPTER XV

A Novel High Temperature Gas Chromatography Unit

HERMAN R. FELTON

Organic Chemicals Department, Jackson Laboratory E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware

INTRODUCTION

A novel, simple, and versatile gas chromatography unit which may be operated at temperatures above 500°C has been developed in this laboratory. Commercial apparatus employing conventional thermal conductivity cells as detectors is limited to temperatures below 300°C due to the nature of the construction (*1–3*). This restricts the use of gas chromatography to the analysis of relatively low-boiling materials. The unit described in this paper was developed in order to expand the application of gas chromatography to include the analysis of high-boiling liquids and solids.

DESCRIPTION OF THE APPARATUS

The essential part of the equipment which makes possible analyses at these elevated temperatures is a thermal conductivity cell which uses model airplane glow plugs as sensing elements (*4*). A schematic diagram of one side of this cell is shown in Fig. 1. Appropriate holes are machined into a metal block to provide a gas stream entrance and exit. The glow plug in Fig. 1 is mounted in a "diffusion" chamber having a small conducting channel to the main gas stream. The most satisfactory plugs for general use were the Champion models VG-2 or VG-3. "Direct pass" units have been made by enlarging the channel and pulling the wire coil out of the plug so it extends into the main gas stream. A photograph of a gas chromatography unit employing this detector is shown in Fig. 2. The body of the unit (1) is a two inch diameter cylinder of steel 6 inches long drilled at the top as indicated. The large metal block serves as a "heat sink" and thus helps in maintaining constant temperature. The carrier gas stream (usually helium) enters the block (2) and passes over a reference glow plug (3). The gas then passes through a "tee" joint to the column (4) which is coiled around the metal body. The "tee" joint is used as the point of introduction of the sample (5). From the column, the gases re-enter the block through a channel which contains a detector glow plug (7) and are then vented (8). A thermocouple well (9) is drilled directly into the body of the block. In use, the unit shown is wrapped with electrical heating tape or placed directly in a suitable oven.

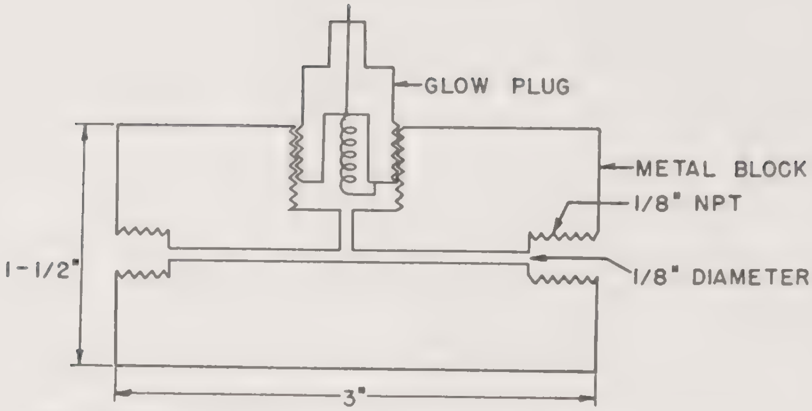


FIG. 1. Glow plug thermal conductivity cell cross section.

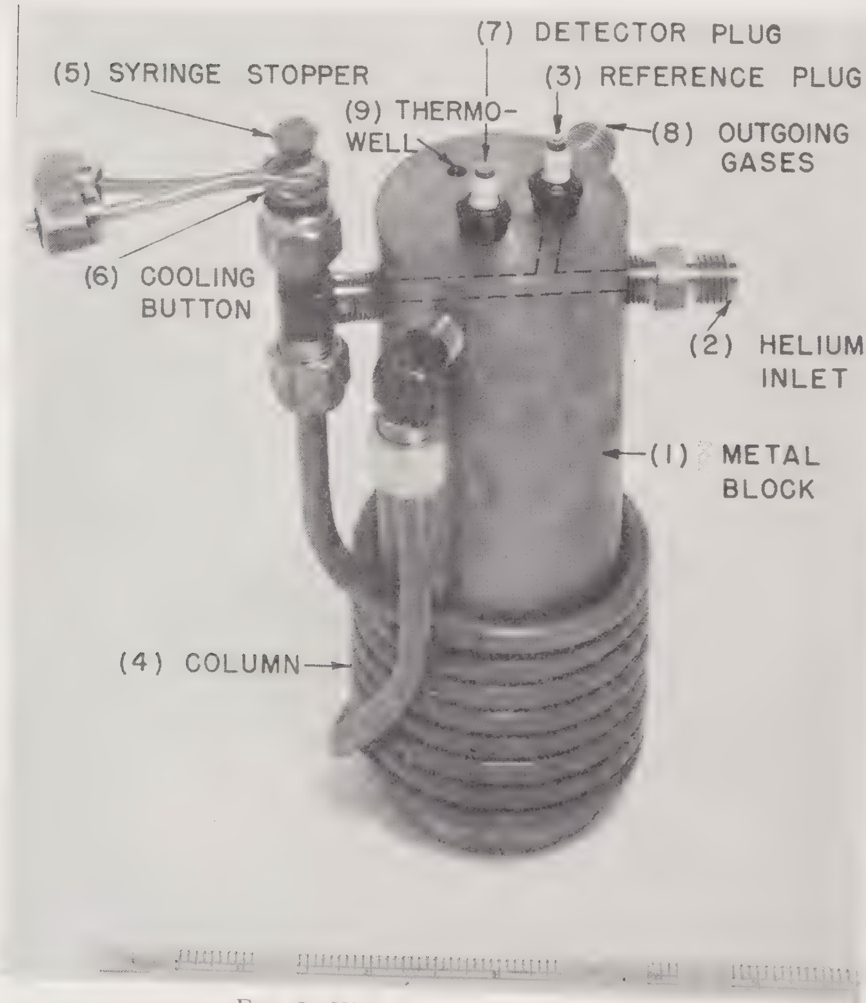


FIG. 2. High temperature unit.

It has been found convenient to use a simple hypodermic syringe for introduction of the sample. In order to keep the rubber syringe stopper from melting or deteriorating at the extreme temperatures of operation, a simple cooling device was designed. This cooling "button" is shown in detail in Fig. 3. A piece of $\frac{1}{4}''$ metal tubing (1) is flared at one end to provide a close fit for a rubber syringe cap. It is then wrapped as closely as possible with $1\frac{1}{2}$ turns of $\frac{1}{8}''$ tubing (2). The volume between this coil and the tube is filled with silver solder (3). The button is then tightened into the "tee" joint of the apparatus with a Swagelok fitting (4). Cold water is circulated through the $\frac{1}{8}''$ tubing and keeps the syringe cap cold while the rest of the chromatography unit is heated.

Since one side of the glow plug wire coil is grounded to the base of the plug, the electrical circuit for the measuring bridge is grounded at this point. The measuring circuit shown in Fig. 4 is a simple bridge which uses the two glow plugs (G,G) and two fixed resistances (R,R) as arms. A zero balance potentiometer (P) is provided. Full wave rectified AC current is used to power the bridge and is provided by a transformer (T) and selenium rectifier (S). The bridge output is picked up directly on a high impedance 5- or 10-mv recording potentiometer. A voltmeter (M) is provided for reading bridge voltage. This is controlled by use of a variable transformer (not shown) in the 110 V AC line. A millivoltmeter may be used in place of a recorder to read bridge output, but has the disadvantage of requiring continuous reading during operation. The entire parts cost of the chromatographic unit and bridge circuit (exclusive of the recorder) is below $100.00.

A major problem that was encountered in high temperature gas-liquid partition chromatography was obtaining a column liquid that was both stable and non-volatile under high temperature operation. The most satisfactory column found for general use was Dow-Corning high vacuum grease (20% by weight) as the partitioning liquid on Celite as the supporting medium. Column lengths of 2 meters were most commonly employed.

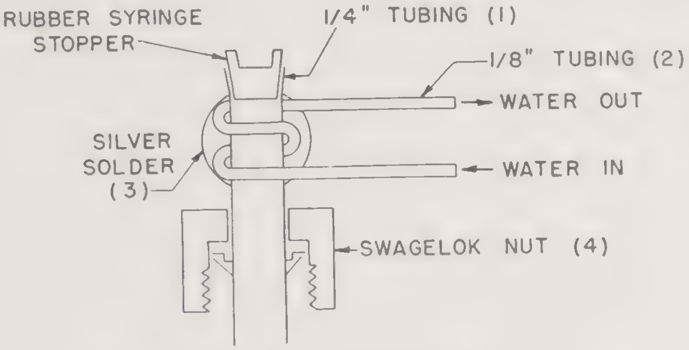


FIG. 3. Cooling button.

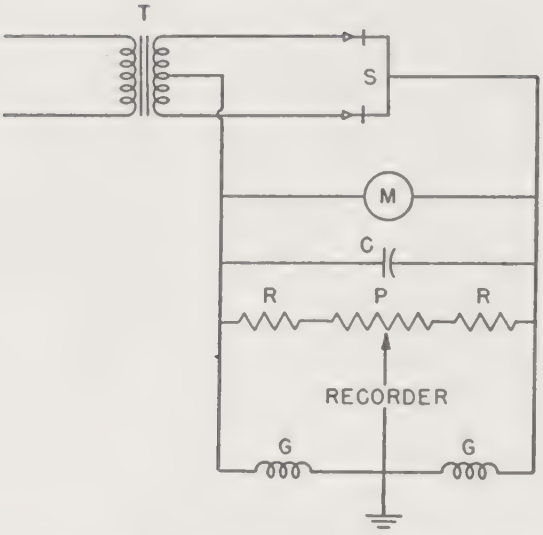


FIG. 4. Electrical circuit for glow plug cell. Key: T, Transformer, 10V, 4A; S, Rectifier UICISIG (radio-receptor); M, Voltmeter (0–3V); R, Resistor, 47 ohms; P, Helipot, 10 turn, 25 ohms; G, Glow plug; C, Capacitor (500 MFD, 50V).

It was found that the columns containing the silicone grease required "conditioning" before they would operate satisfactorily. This was accomplished by heating the apparatus to 400°C and maintaining this temperature for 2–3 hours with a helium flow of 25 ml/minute. If this "conditioning" was omitted, no separations could be accomplished and the instrument response after injection of a sample was a series of erratic peaks which could not be reproduced. No satisfactory explanation of this behavior has been found, although some of the difficulty may result from low boiling materials in the high vacuum grease.

Calibration and Response

Units of the design described above have performed excellently at temperatures from 25°C to 500°C over several months. The sensitivity of response is comparable to that of other "hot wire" thermal conductivity cells. Above 300°C standard thermistors have no application and therefore cannot be directly compared with glow plug units. The signal obtained from 0.25 ml of air has been used as a calibration for response. Figure 5 shows the response in millivolts of one such unit to this amount of air as a function of temperature. The curve shown was made with 2.0 volts applied across the bridge, at a helium flow of 25 ml/minute on a 2-meter column. These conditions are typical of those under which many analyses were run. Using the response at 100°C (2.10 mv) as a reference point, there is a decrease of 15% in response at 300°C and of 33% at 500°C. Under these same conditions, using a one millivolt recorder, the limit of detection of the instrument at 500°C is 0.015 ml of air.

By increasing the voltage on the bridge to 3.0 volts, the instrument response may be more than doubled over that obtained at 2.0 volts. Figure 6 shows the effect of bridge voltage on response to 0.25 ml of air at 400°C.

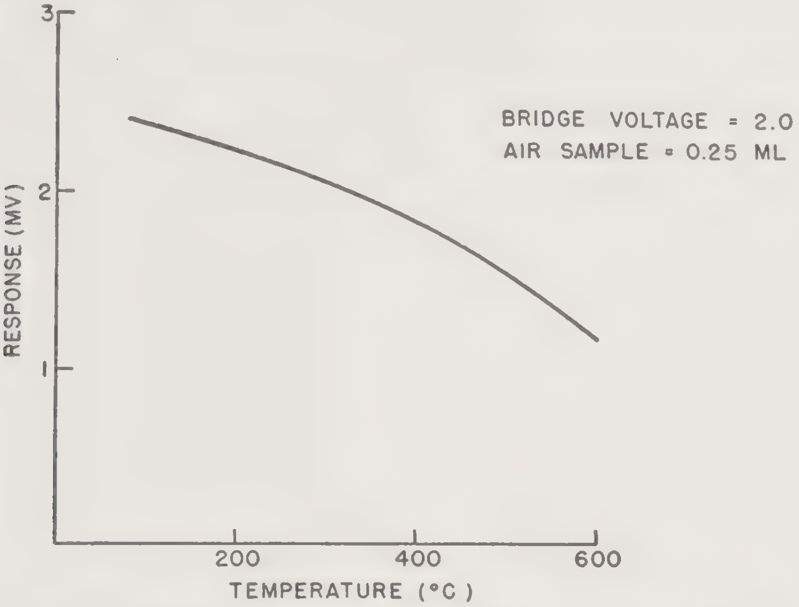


FIG. 5. Effect of temperature on the chromatograph response.

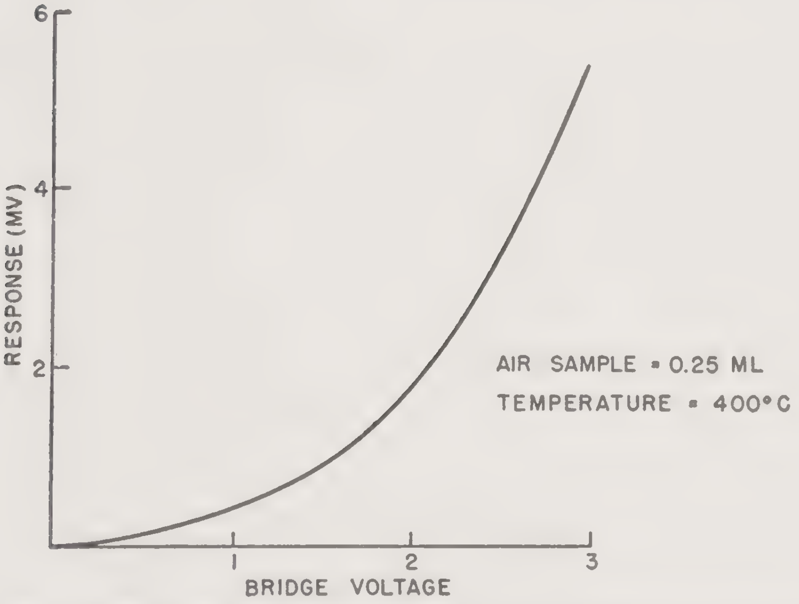


FIG. 6. Effect of bridge voltage on the chromatograph response.

The response increases with increasing voltage and, as the curve of Fig. 6 suggests, is proportional to the square of the voltage (or the power input to the bridge). The circuit was not operated above 3.0 volts since the glow plugs are designed by the manufacturer for use at 1.5 volts.

The noise level and short-term drift of the instrument were satisfactorily low. Under operating conditions from 300° to 500°C with 1.5 to 2.5 volts across the bridge and at a helium flow of 25 ml/minute, the noise level and drift over a half-hour period were from 50 to 100 microvolts.

Experience with glow plug chromatography units shows that they offer several advantages over conventional equipment. While most present commercial apparatus is limited to 250–300°C (*1–3*), the glow plug apparatus has performed satisfactorily above 500°C. The units are versatile and have been operated for routine analysis at 25°C as well as at the higher temperatures. Easy part replacement is another advantage. A new plug can be installed in a few minutes, while the unit is maintained at operating temperature. The glow plugs are mass produced so uniformly that little or no disturbance of the bridge occurs on replacement. The equipment may be operated under vacuum or pressure with no leakage problem.

ANALYSES USING THE GLOW PLUG UNIT

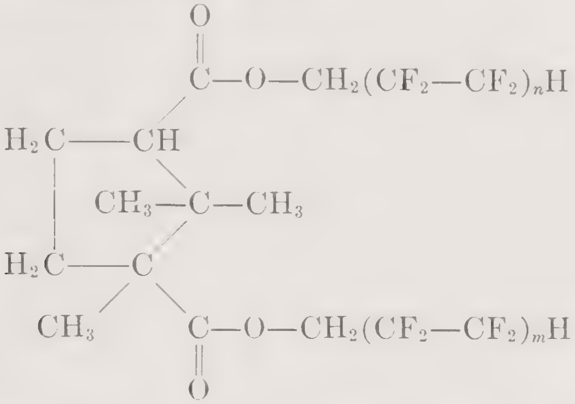
This high temperature gas chromatography unit has been applied to many problems of analysis, typical of which are (1) the analysis of mixtures of high boiling fluoroesters of camphoric acid, (2) the separation of the α- and β-positional isomers of *N*-phenylnaphthylamine, and (3) the determination of mono, di, and tri functionality of tolueneisocyanates. These analyses, which are described below, were carried out under the following conditions:

Column material	25 % Dow-Corning high vacuum grease on Celite
Column length	2 meters
Carrier gas	Helium
Carrier gas flow	25 ml/min
Bridge voltage	1.75 volts
Recorder range	Variable
Temperature	Variable
Sample Size	0.01 ml liquid

In those cases where the sample material was solid, such as α- and β-*N*-phenylnaphthylamine, a solution was prepared, usually in acetone or chloroform. Solutions were also used when the substance being analyzed was a viscous liquid. An amount of solution containing 0.01 ml of the solute was used as a sample. A volatile solvent was selected which had a short retention time so that it would not interfere with the elution of sample components.

Camphorate Esters of Fluoroalcohols

An outstanding application of high temperature gas chromatography was demonstrated in the analysis of mixtures of the fluoroalcohol esters of camphoric acid. Prior to the development of the glow plug unit, there was no successful method for performing this analysis. The structure of this particular class of esters is given below:



These materials are liquids of remarkable thermal stability and high boiling point and have been proposed as high temperature lubricants for jet aircraft. The estimated normal boiling points range from about 320°C where each side chain has 3 carbon atoms (n and $m = 1$) to about 460°C where the side chains are derived from the C_{11} alcohol (n and $m = 5$). The latter ester (which is simply referred to as the diC_{11} compound) has a molecular weight of 1228.

In order to calibrate the chromatograph, pure standards and a synthetic mixture of the camphorate di-esters prepared to contain equal weights of the C_3, C_5, C_7, C_9, and C_{11} diesters were used. The chromatogram recording shown in Fig. 7 was obtained for this standard mixture at 325°C in a 2-meter column at a carrier gas flow of 25 ml/min. The small peak between the diC_9 and diC_{11} esters was for the C_9C_{11} mixed ester which was found as a contaminant in the particular samples of these latter diesters.

From this chromatogram standard, ratios of peak heights of equal weights of the various esters can be obtained. Arbitrary selection of the height of the diC_7 peak as a reference gives the following relative peak height ratios:

$$diC_3/diC_7 = 2.61$$

$$diC_5/diC_7 = 1.52$$

$$diC_7/diC_7 = 1.00$$

$$diC_9/diC_7 = 0.57$$

$$diC_{11}/diC_7 = 0.36$$

Measurements on the pure materials showed that the peak heights were proportional to sample size. In order to calculate quantitative results for an unknown mixture, the following procedure was used: (1) the peak height of each ester present was measured, (2) each peak height was divided by the relative peak height ratio for the particular ester to give an ester "quotient", (3) all of the results obtained from Step 2 were added to give a "total", and (4) each ester "quotient" was divided by this "total" and multiplied by 100 to give the weight per cent of each ester in the sample (normalization to 100 % content). Mathematically, this can be expressed as:

$$\text{Weight \% Ester}_1 = \frac{\dfrac{H_1}{R_1} \times 100}{\displaystyle\sum_{i=1}^{i=n} \frac{H_i}{R_i}}$$

where H is the peak height for an ester and R is the relative peak height ratio for that ester. It was found that a similar procedure applied to peak areas gave results within 5 % of those obtained from peak heights. A series of analyses showed that the precision of the peak height method was approximately 1 % absolute.

A plot of the logarithm of the retention times for the chromatogram

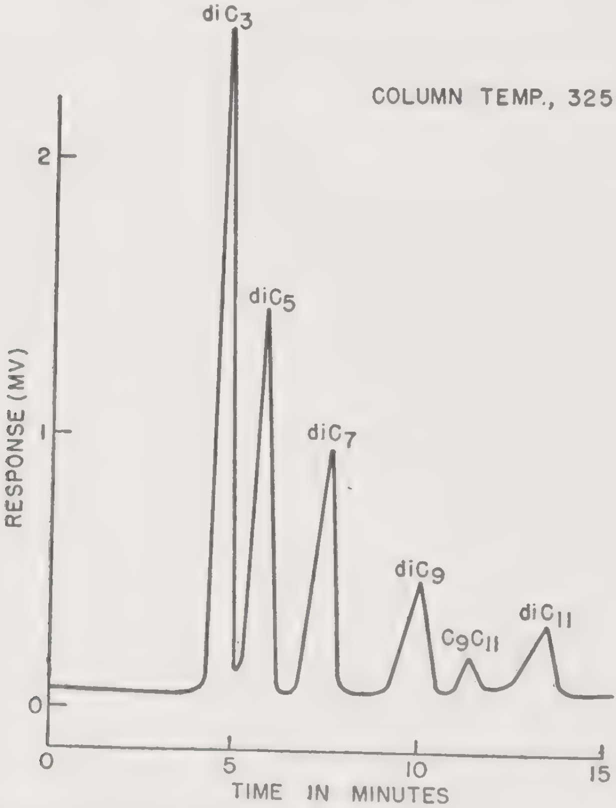


Fig. 7. Chromatogram of fluoroalcohol camphorates.

recording shown in Fig. 7 as a function of the number of carbon atoms in the ester chains gives the familiar straight line seen in Fig. 8. Shown also on this plot by circles are the points for the mixed esters C_5C_7 and C_7C_9. Figure 8 indicates that the diC_7 ester and mixed C_5C_9 ester would not be resolved, since each has a total of 14 carbon atoms in the ester chains (and the same molecular weight).

The analysis of a mixture of esters gave the chromatogram recording shown in Fig. 9. This mixture was made by esterifying the camphoric acid with an equimolar mixture of the C_5 and C_9 alcohols. The molar ratios found for the product mixture were 1.0:2.0:1.2 for the diC_5, C_5C_9, and diC_9 esters. Since the 1:2:1 ratio was obtained, as would have been predicted on a statistical basis, it could be concluded that (1) either the reac-

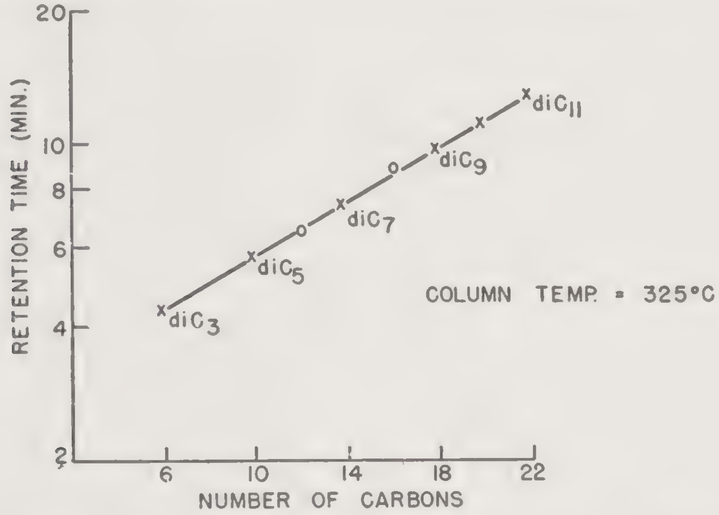


FIG. 8. Effect of camphorate ester size on retention time.

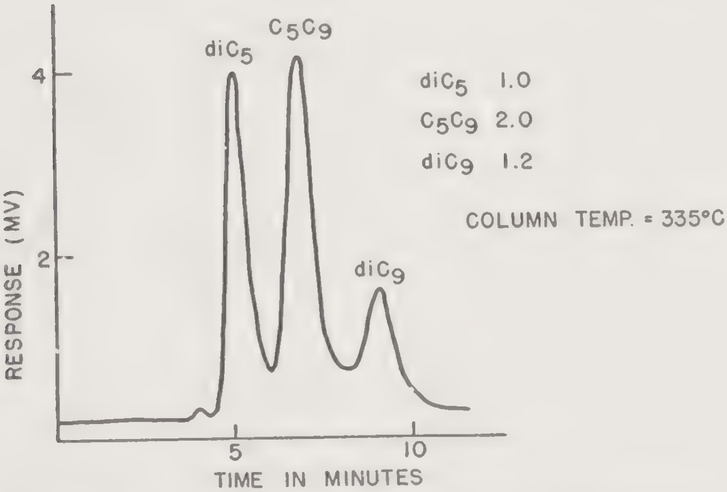


FIG. 9. Chromatogram of mixed C_5C_9 camphorate esters.

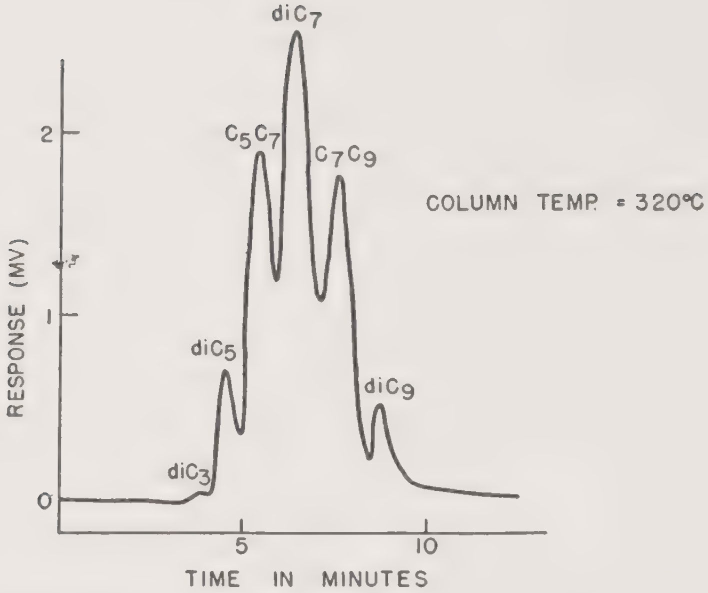


FIG. 10. Chromatogram of camphorate ester jet lubricant.

tion rates of the various alcohols with the acid were nearly the same or (2) the rate of ester interchange was rapid compared to the rate of esterification.

Figure 10 shows the chromatogram recording of a complex mixture of these esters after use as a jet lubricating oil. From the peak heights and retention times it is possible to obtain both a qualitative and quantitative analysis of this material. Prior to the use of the high temperature gas chromatography unit, only physical means, such as viscosity measurement, could be used to characterize this lubricating oil before and after use. The chromatographic technique made it possible to follow any change in chemical composition or ester proportions had they occurred during actual engine operation.

Isomers of N-Phenylnaphthylamine

A second analysis for which high temperature gas chromatography proved useful was in the separation and estimation of the α- and β-isomers of *N*-phenylnaphthylamine. These materials are solids at room temperature, melt at 62°C and 108°C, respectively, and boil above 400°C. Since the samples were solid, they were run in acetone solution. At 370°C the chromatogram shown in Fig. 12 was obtained. Calibration with pure isomers indicated that the mixture shown in Fig. 11 is 23% (by weight) α-*N*-phenylnaphthylamine and 77% β-isomer. The acetone solvent appeared as a sharp peak at about 2 minutes.

The absence of any small extraneous peaks was taken as evidence that no thermal decomposition of the injected materials had occurred. If a

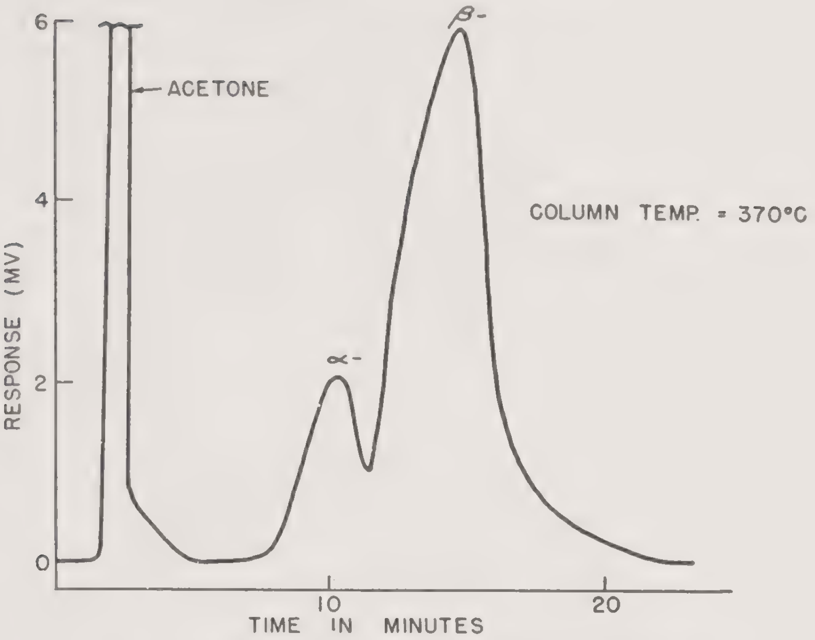


FIG. 11. Chromatogram of *N*-phenylnaphthylamines.

compound did decompose at the temperature of operation, we should expect to get some separation of the pyrolysis products in the column, which would appear as separate peaks. No evidence of decomposition has been observed at temperatures below 400°C in the apparatus. However, no attempts have yet been made to resolve this question by collection and examination of the eluted peaks. The low partial pressure of the solute in the inert gas undoubtedly contributes to this high stability.

Toluene Isocyanates

Organic diisocyanates are becoming increasingly important as intermediates in chemical manufacture. In the analysis of toluene diisocyanate, it is desirable to have a method for determining the presence of any monoisocyanate or triisocyanate. The separation of these materials can be accomplished at 250°C on a 2-meter column. Under these conditions the monoisocyanate isomers were obtained as a single peak, and the diisocyanate isomers as a separate single peak. The retention times for pure standards are shown below. The isomers included are only those expected to be present in the samples.

Compound	Retention Time (Minutes)
o-Tolueneisocyanate	2.37
p-Tolueneisocyanate	2.35
Toluene-2,4-diisocyanate	3.70
Toluene-2,6-diisocyanate	3.67
Toluene-2,4,6-triisocyanate	5.87

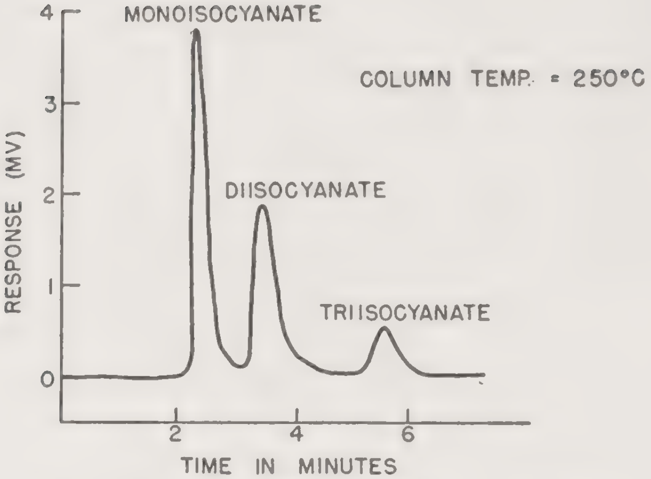


FIG. 12. Chromatogram of toluene isocyanates.

Separation by the number of functional groups present was excellent. The chromatogram recording of a synthetic mixture of equal weights of mono, di, and triisocyanates is shown in Fig. 12. Under these conditions it is estimated that the limit of detection of the monoisocyanate is about 0.1 % and the triisocyanate about 0.5 %.

SUMMARY

A high temperature gas chromatography unit capable of operating above 500°C has been used to analyze high-boiling liquids and solids. Three examples of analyses which may be performed with this equipment have been given to illustrate the applicability of gas chromatography to the analysis of materials of very low volatility. It is expected that the apparatus will find wide application in many fields.

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2. Perkin-Elmer Corp., Norwalk, Connecticut, Bull., "Vapor Fractometer—Model 154B." (1957).
3. Fisher-Scientific Co., Pittsburgh, Pennsylvania, Bull. FS-255 (1957).
4. H. R. Felton and A. A. Buehler, A high temperature thermal conductivity cell, to be published in *Anal. Chem.*

DISCUSSION

MOBERG (*Aerojet-General Corp., California*): Have you experienced any difficulties in condensation of sample within your instrument?

FELTON: No, we have not had any trouble from condensation. In several cases we made some checks to determine if the number of moles of substance that came through were the same as that which were injected. In replacing the serum cap, occasionally we will run a pipe cleaner through the tube. Occasionally it comes out somewhat brown, but not enough to worry about.

GOBRAN (*Thiokol Chemical Corp., New Jersey*) Could you separate diisocyanate isomers with the column you used?

FELTON: You cannot get separation of the isocyanates under the conditions that I showed in the slide pertaining to that column. Under other conditions, however, we have been able to separate the 2, 4, the 2, 6, the 2, 3, and the 3, 4 isomers of the diisocyanates. We have done no work on the polymeric isocyanates.

CHAPTER XVI

Analysis of Ester-Type Plasticizers by Gas-Liquid Chromatography

J. S. LEWIS AND H. W. PATTON

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee

INTRODUCTION

There is a need for a rapid, reliable, and simple method of analyzing for various plasticizers in small amounts of material. Ester-type plasticizers are usually identified by saponification and subsequent characterization of the acids and alcohols produced. This procedure requires a great deal of time and cannot always be done when the sample size is very small. Furthermore, it generally results in identification of only the major components present. Burns reported that paper chromatography is particularly suitable when only small amounts of material are available for analysis, but the results obtained are often inconclusive (*1*). Infrared absorption spectroscopy is very satisfactory for identifying the major component of the sample or for determining the structural groups present. However, it is not particularly suitable for analyzing minor components of a mixture.

Gas chromatography has been successfully applied to a variety of problems. Most of the work has dealt with the analysis of gases and relatively low-boiling liquids. However, at present it is possible to operate heated gas chromatographic columns to analyze for materials boiling as high as 400 to 450°C. Therefore, it seemed probable that ester-type plasticizers could be analyzed by this method.

In this paper we shall describe the apparatus and materials used in developing a gas-liquid chromatographic method of analysis for plasticizers. We shall give specific examples of its application to analyses that are very difficult to perform by other means. Samples of the extract from plasticized molding compositions were analyzed, and the plasticizers were tentatively identified on the basis of their elution times. Thus, it was possible to determine the plasticizers used in the manufacture of the molding compositions. The method was also applied to the identification of the materials present in relatively pure substances and in mixtures available as commercial plasticizers.

APPARATUS

A block diagram of the apparatus is shown in Fig. 1. Helium, the carrier gas, flowed through the system continuously. The flow rate was indicated by flowmeters and controlled by needle valves (Hoke Inc., 2RB280). Constant pressure was maintained at the inlet to the flowmeters by a Climax Regulator (Black, Sivalls, and Bryson, Inc., Type 73-26). The flow rate was set at 50 ml/min. with the columns at room temperature, and the settings on the needle valves were not changed as the columns were heated. A thermal conductivity cell [Gow-Mac Instrument Co., model No. 9193 (TE-II)] was used as the detector. Separate columns were connected to the reference and sample channels of the cell. While a sample was being eluted from one column, the carrier gas for the reference channel of the cell flowed through the other column. Thus, it was possible to operate two columns, one at a time, with a given cell. During the exploratory experiments this arrangement was used to advantage in operating two columns of different lengths or at different temperatures with the same cell.

Figure 2 shows the column, vapor jacket, and sample-injection section. Condensing vapors from a boiling liquid were used to maintain the column at a constant temperature. The sample-injection (preheater) section and the thermal conductivity cell were heated by wrapping them with nichrome wire and supplying electrical energy from a Powerstat variable transformer. The preheater section was operated at a temperature greater than that of the column. However, the temperature had to be low enough to avoid appreciable thermal degradation of the samples being analyzed. For instance, bis(2-ethylhexyl) phthalate was quite stable when the preheater was at 580°C. On the other hand, bis(2-ethylhexyl) isophthalate was almost completely decomposed at 580°C. It was partially decomposed at 440°C., but was not appreciably decomposed at 330°C.

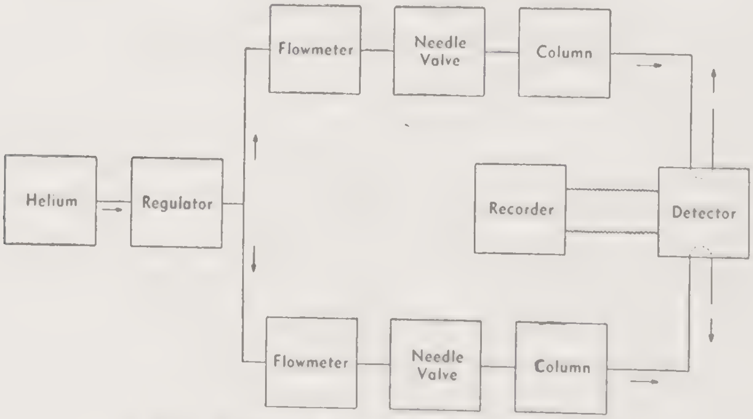

FIG. 1. Block diagram of apparatus.

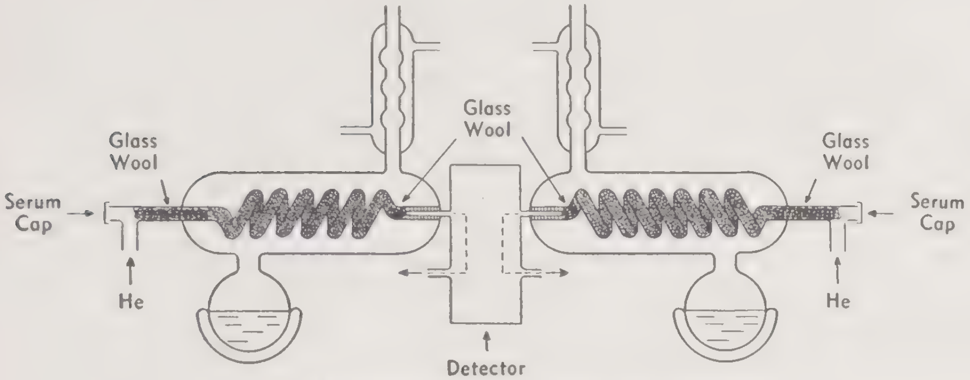

FIG. 2. Arrangement of columns and detector.

The glass columns, 0.5 cm in diameter by 60 or 120 cm long, were helical and were connected to the $3/16$-in. metal tube of the thermal conductivity cell with 0.5-in. lengths of $5/16$-in. o.d. x $1/16$-in. wall silicone rubber tubing. The silicone rubber tubing formed a gasket between the outside of the tube from the thermal conductivity cell and the inside of the gas-liquid column. In operating the glass columns at temperatures in the region of 300°C., it was very difficult to find a completely satisfactory means of attaching the columns to the cell. Deterioration of the silicone rubber tubing used as a seal between the column and cell was observed after approximately one month of continuous operation.

MATERIALS

Gas-liquid columns were prepared using a procedure previously described (*2*). In order to minimize the pressure drop across the columns, the kieselguhr (Johns-Manville, Celite 545) was screened, and only that portion retained on a 50-mesh sieve was used. This material was washed with water to remove the dust and then dried in an oven overnight at about 130°C. The high-boiling liquid used to prepare the column was Apiezon Oil K (James G. Biddle Co.).

The high-boiling liquid was not mixed with the Celite directly, but was applied from solution in a volatile solvent. A solution of 2.0 g of the high-boiling liquid in 12 ml of pentane was poured with constant stirring onto 4.7 g of Celite. Ideally, the Celite should be completely wet, with no excess solution. The pentane was then allowed to evaporate, leaving the Celite uniformly impregnated with the high-boiling liquid.

The material thus prepared was packed into the columns by agitation from an electric vibrator. Glass-wool plugs were used to keep the packing in place.

METHODS

Samples to be analyzed were injected into the preheater section through a rubber serum cap with a syringe having a 0.25 ml capacity. The volume of sample used was 0.01 ml or less. The sample was vaporized in the preheater section and swept onto the column by the carrier gas stream. Components of the sample were separated and were detected by the thermal conductivity cell as they came from the column. The output from the cell was fed to a potentiometer recorder which automatically plotted the chromatograms of detector response vs. time.

Quantitative determination of the various components present in the plasticizers was based on the areas under the elution peaks as estimated by multiplying the peak height by the width of the peak at one-half of its height. The sample composition was calculated assuming the weight fraction of each component to be equal to its peak area divided by the total area of all the peaks. Since the thermal conductivities of ester-type plasticizers are very different from that of helium, the results based on this assumption are likely to be good. Better accuracy might be obtained by calibrating with mixtures of known composition.

ELUTION TIMES FOR KNOWN MATERIALS

The chromatograms of some materials used as plasticizers are shown in Fig. 3 to indicate the number of impurities present. These chromatograms were produced using a column 60 cm long maintained at a constant temperature by condensing vapors from boiling dimethyl phthalate, which

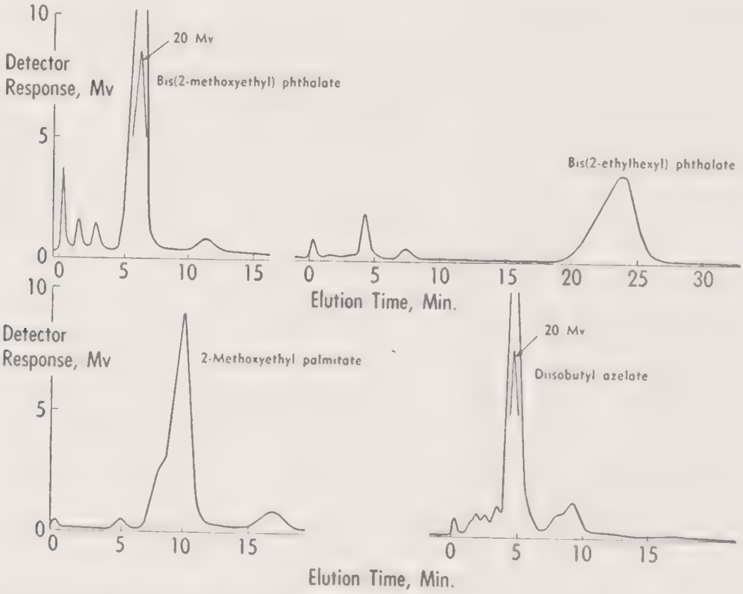

FIG. 3. Chromatograms of some materials used as plasticizers.

boils at approximately 283°C. The recorder range was 10 mv except where indicated, and the chart speed was 16 in./hr.

Relative elution times of several compounds used as plasticizers were determined and are listed in Table I. Because some of the compounds

TABLE I

RELATIVE ELUTION TIMES FOR KNOWN MATERIALS

(Dibutyl Phthalate = 1.0)

Material	Relative Time
Triethyl phosphate	0.05
Dimethyl phthalate	0.24
Glycerol tripropionate	0.25
Diethyl phthalate	0.35
Diisobutyl phthalate	0.74
Diisobutyl azelate	0.91
Dibutyl phthalate	1.0
Bis(2-methoxyethyl) phthalate	1.3
Dibutyl isophthalate	1.4
Isobutyl palmitate	1.7
Dibutyl sebacate	1.7
2-Methoxyethyl palmitate	1.9
Bis(2-ethylbutyl) phthalate	2.2
Bis(2-ethylhexyl) adipate	3.1
Diisoocytl adipate	3.1
Triphenyl phosphate	5.1
Bis(2-ethylhexyl) phthalate	5.1
Diethylene glycol dibenzoate	5.4
Bis(3,5,5-trimethylhexyl) phthalate	7.6
Bis(2-ethylhexyl) isophthalate	9.1
Tris(*m*-tolyl) phosphate	9.5

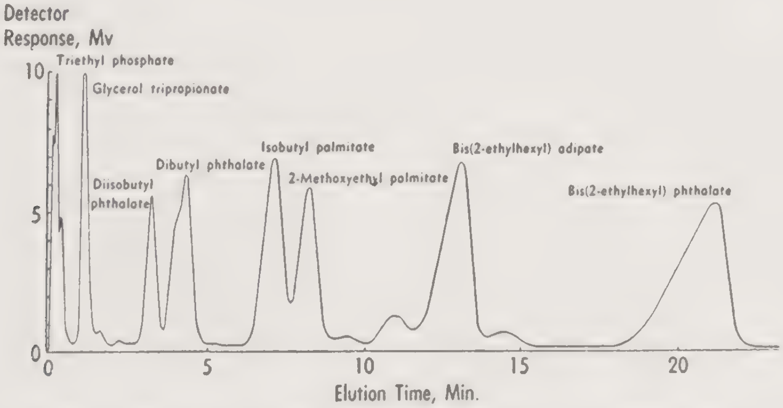

FIG. 4. Separation of a synthetic mixture of plasticizers.

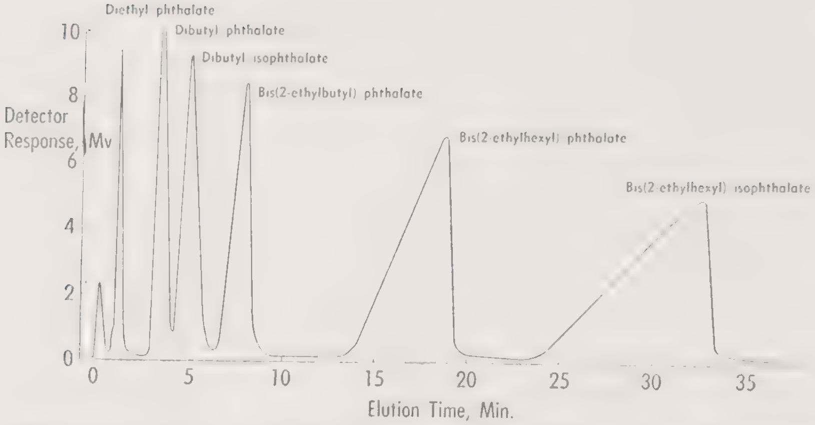

FIG. 5. Separation of a synthetic mixture of phthalates and isophthalates.

produce asymmetrical elution peaks, their elution times vary with sample size. Hence, values for these compounds are only approximate.

Naturally, it would not be possible to separate each of the materials listed from a mixture containing all of them. A synthetic mixture of some of these materials was prepared, and the chromatogram of the mixture is shown in Fig. 4. These compounds were arbitrarily chosen to illustrate the separation that could be obtained with a relatively complex mixture. Separate peaks for each component in the mixture were observed. The peaks on the chromatogram, other than those labeled, are due to impurities in one or more of the esters used to prepare the mixture.

A chromatogram of a synthetic mixture of various phthalates and isophthalates is shown in Fig. 5. It was interesting to note that the phthalates were eluted from the columns sooner than the respective isophthalates. In the case of *o*-xylene (b.p. 144.4°C.) and *m*-xylene (b.p. 139.1°C.), the ortho isomer is eluted from the column after the meta isomer.

Analysis of the Extract from Plasticized Molding Compositions

The method was applied to the analysis of several samples of extracts from plasticized molding compositions. The chromatograms shown in the following figures were produced using a 120-cm column packed with the Celite-Oil K packing. Condensing vapors from boiling dimethyl phthalate maintained a constant temperature in the column.

A chromatogram was run on the extract obtained from a commercial molding composition to obtain the curve shown in Fig. 6. On the basis of their elution times the materials were identified as diisobutyl phthalate and diethylene glycol dibenzoate. They were present to the extent of 19 and 75%, respectively.

Methods of gas-liquid chromatography are very satisfactory for determining whether a specific plasticizer was used in the manufacture of various molding compositions. These methods are particularly useful when only a small amount of extract can be obtained, as is the case with extracts from a fountain pen barrel, button, toy whistle, or other small molded object. Three samples of this nature were run, and the chromatograms are shown in Fig. 7. The problem was to determine if dibutyl sebacate had been used as the plasticizer. The three chromatograms were compared

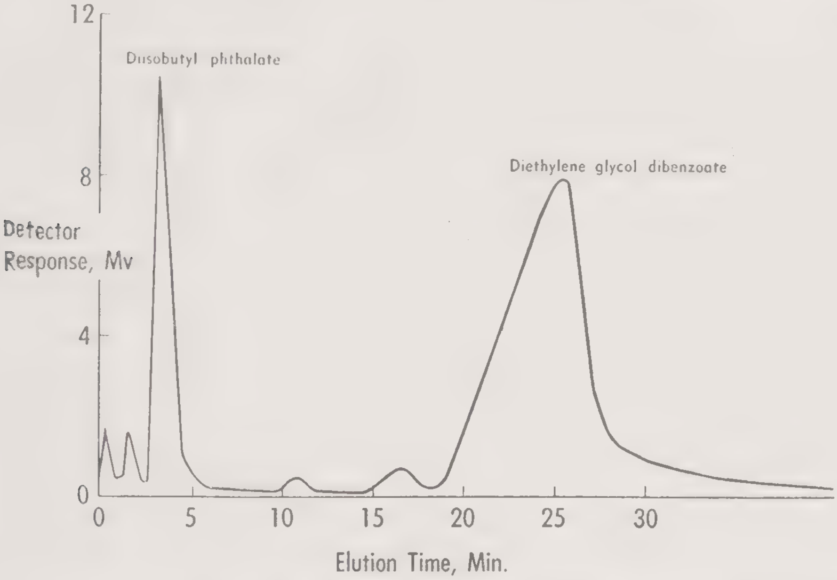

FIG. 6. Analysis of plasticizers extracted from a commercial molding composition.

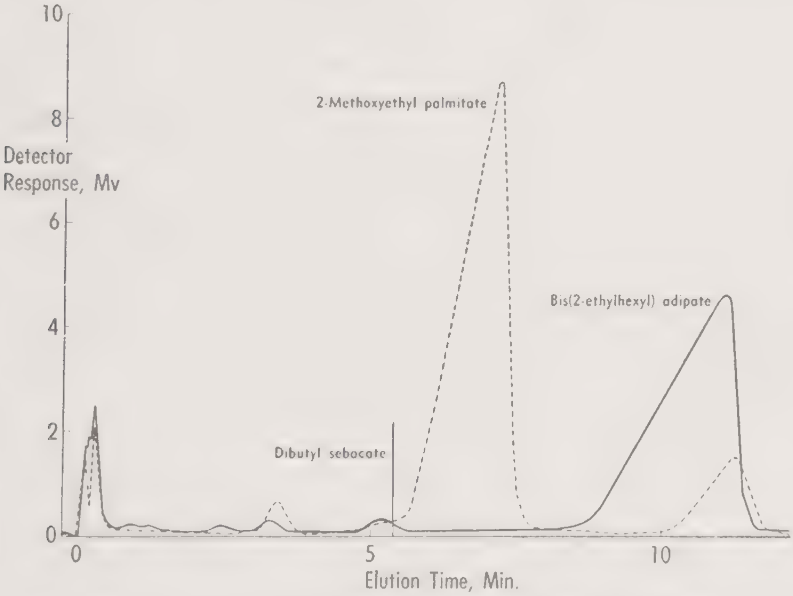

FIG. 7. Comparison of extracts from three plastics.

with the chromatogram of dibutyl sebacate. The broken curve represents two of the samples which were identical. The elution time of the major component was the same as that for 2-methoxyethyl palmitate. The main component of the third sample was eluted from the column at the time for bis(2-ethylhexyl) adipate. None of the samples contained dibutyl sebacate, which would be eluted at the time indicated.

IDENTIFICATION OF MATERIALS IN COMMERCIAL PLASTICIZERS

Methods of gas chromatography and infrared absorption spectroscopy were used to identify the materials present in a commercial plasticizer.

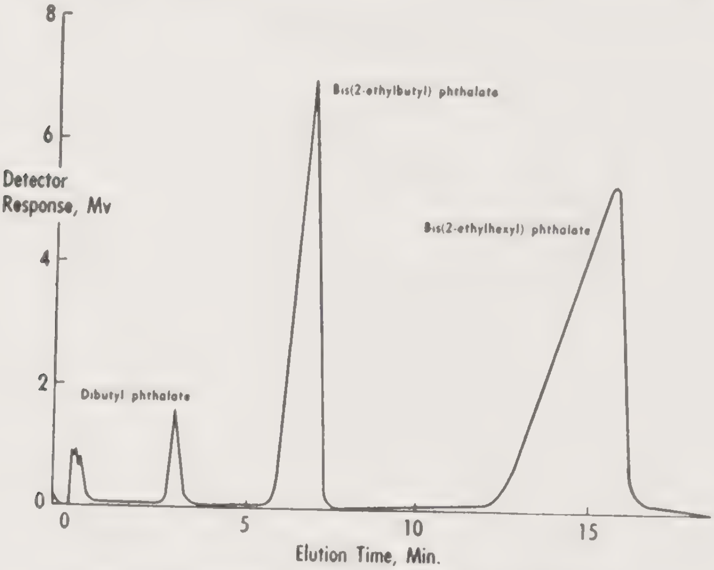

FIG. 8. Analysis of a commercial plasticizer.

Infrared studies indicated that the sample was bis(2-ethylhexyl) phthalate. The chromatogram shown in Fig. 8 indicates that at least two major components and one minor component were present. Elution times of the major components were identical with that of bis(2-ethylbutyl) phthalate and bis(2-ethylhexyl) phthalate, respectively. The elution time of the minor component detected was that for dibutyl phthalate. The composition of this commercial plasticizer was calculated to be 64.0% bis(2-ethylhexyl) phthalate, 30.9% bis(2-ethylbutyl) phthalate, 2.9% dibutyl phthalate, and 2.2% low-boiling impurities.

SUMMARY

Methods of gas chromatography were very satisfactory for the analysis of plasticizers, and they were especially useful when only small amounts of material were available. It was also possible to identify the components

in commercial plasticizers from their chromatograms. In addition to the qualitative analysis of plasticizers in various molding materials, the method can probably be used for such problems as determining the effect of weathering on plasticizers in plastics, determining the effect on plasticizers of various stages in the manufacture of plastics, and determining the impurities and intermediate products produced in the manufacture of materials used as plasticizers.

Acknowledgment

The authors are indebted to Mr. Roy O. Hill, Jr., Tenite Development Department, for supplying the samples of extracts from plasticized molding compositions.

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CHAPTER XVII

An Instrument Designed for High Temperature Gas Chromatographic Analysis

B. W. TAYLOR

Fisher Scientific Company, Pittsburgh, Pennsylvania

Gas chromatography has proven to be a very important and powerful technique in the analytical field with most of the work concentrated at temperatures below 150°C. There is still much work to be done at these lower temperatures and it is only a matter of time before some of the more difficult problems will be solved.

Since the technique is expanding at a very fast rate, it is a natural step into higher temperatures for higher boiling materials. This interest has brought about the development of an instrument to handle a much wider variety of components. If the problem of higher temperatures only involved increasing the heat input our job would have been relatively simple. However, this was not so.

With the desire to employ gas chromatography for the analysis of higher boiling materials a completely new instrument had to be designed.

In order to satisfactorily analyze the very high boiling materials, it is important that the sample be vaporized quickly. This permits the column and cell to be operated at a somewhat lower temperature and still give resolution. With this fact in mind, we have attempted to design an instrument that will cover a wide temperature range and maintain high sensitivity over the entire temperature range.

The following features are incorporated in this instrument:

1. Temperature range
    - A. Cell bath thermistor regulated up to 200°C.
    - B. Column bath regulated from below room temperature to 300°C.
    - C. Flash evaporator controlled up to about 425°C.
2. Sensitivity
    - A. Newly designed thermistor thermal conductivity cell.
    - B. 0–2 mv recorder.
    - C. Stepwise sensitivity control.
    - D. Coarse and fine balance control.
3. Transistor regulated power supply delivering up to 100 ma.
4. New readout trace for integrator.
5. Reproducible sample introduction system for high temperature work.

The above features are shown in detail on a block diagram of the chroma-

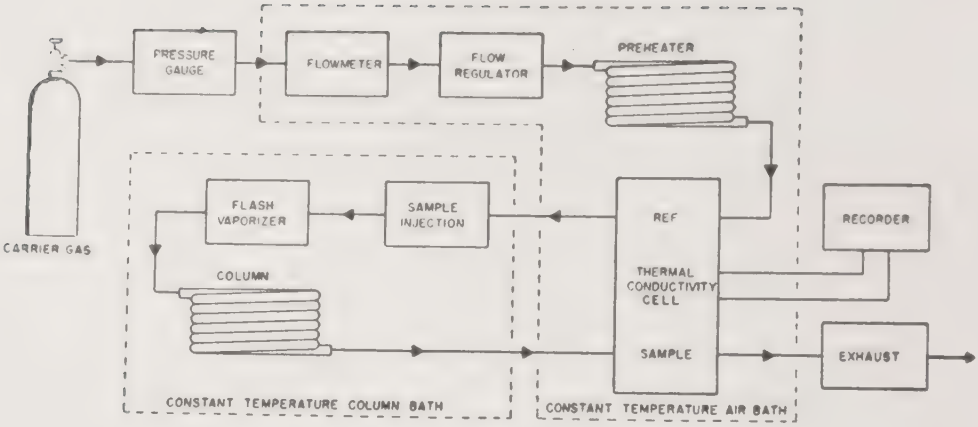


Fig. 1. Block diagram.

tographic system in Fig. 1. This system is very much like some other chromatographic systems in that the cell is in one temperature controlled air bath and the chromatographic column is in another. The carrier gas first passes through a flowmeter which is calibrated for helium at approximately 20 psi at 25°C. It passes on through a flow regulator into a preheater coil and into the reference side of the thermal conductivity cell. From the cell the gas passes through $1/16''$ O.D. tubing, out of the cell bath and into the sample introduction system which is in the column bath. Then out through an orifice of the introduction system into the "flash evaporator" and on into the chromatographic column. The exhaust of the column passes through $1/16''$ O.D. tubing into the cell bath, and into the sample side of the thermal conductivity cell it is then exhausted to the atmosphere or a sample collecting device.

The chromatographic system is housed in two separate baths and each, of course, is temperature regulated. This makes it possible to change columns without affecting the thermal equilibrium of the conductivity cell.

Let us discuss the cell compartment temperature control. Experimental evidence has shown that the temperature of this compartment must be controlled within very narrow limits. This has been accomplished by employing a thermistor sensing element, and a magnetic amplifier to operate a relay, which cycles a heater. A temperature range switch having four positions, (50, 100, 150, and 200°C), allows one to operate this chamber at a temperature which gives maximum sensitivity in line with minimizing the possibility of the accumulation of condensate in the cell itself. This bath is attached to the front panel. Such arrangement allows the whole drawer assembly to be withdrawn to exchange columns without affecting the cell compartment temperature equilibrium.

The column bath, on the other hand, is designed with five sides that are

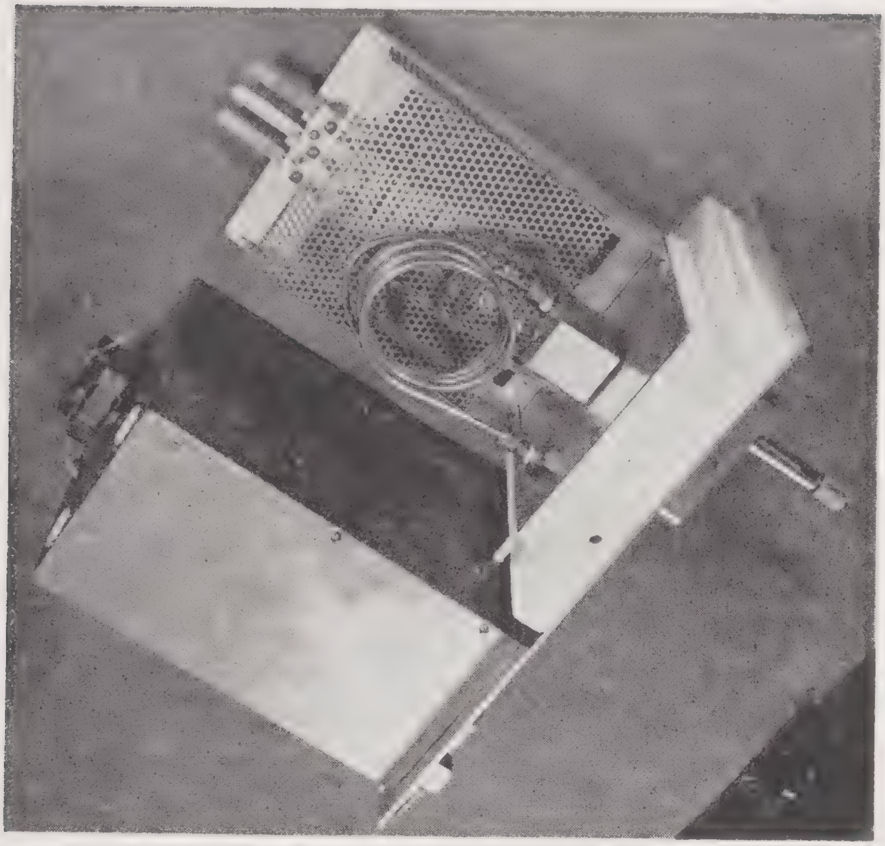


Fig. 2. Drawer assembly.

an integral part of the main cabinet; but, the column, heaters, and thermostats are part of the drawer assembly as shown in Fig. 2.

The temperature of the column bath is controlled by a series of preset bimetallic thermoregulators from 50 to 300°C in intervals of 25°. There are two wire-wound heaters, one being controlled by a Powerstat as a constant heater, and a smaller one cycled by the thermoregulators. A cooling coil is attached to the column bath by which the chamber can be cooled below the ambient temperature by passing a collant through this coil. This is desirable for the analysis of low boilers or when it is desired to reduce the bath temperature quickly.

The sample introduction system is similar to that developed by the Esso Research Laboratories, Baton Rouge, Louisiana. It differs in that we have incorporated the orifice into a "flash evaporator" (Fig. 3). When the sample is introduced into the system it comes in contact with a heated section, whose temperature can be considerably above the column temperature, before it enters the column. This contributes to rapid sample vaporization, which has two virtues. The sample may enter the column in the vapor phase, and, the possibility of slow vaporization which results in broad or multiple peaks is reduced.

In order to heat the "flash evaporator", it is surrounded by a metal block of large mass in which a 100 watt cartridge heater is located. The temperature of the block is read with a dial thermometer which can be slid in or out, permitting the thermometer to indicate block or bath temperature. Since close temperature control of the column is not required as much as of the cell, a Powerstat is used to control the heat input to the block, which can be heated up to about 425°C, or 125°C above the maximum column temperature.

The high sensitivity is obtained by a combination of conditions. First, we have incorporated a 0–2 mv recorder into the instrument. The thermal conductivity cell has been redisigned, the sample thermistor being located directly in the stream and the cell cavity volume has been reduced to approximately 0.1 ml. The current input to the cell is controlled to give high sensitivity at all bath temperatures.

A new transistor power supply has been developed which can deliver up to 100 ma, making it possible to introduce more current to the thermistors at the higher temperatures, thereby maintaining high sensitivity.

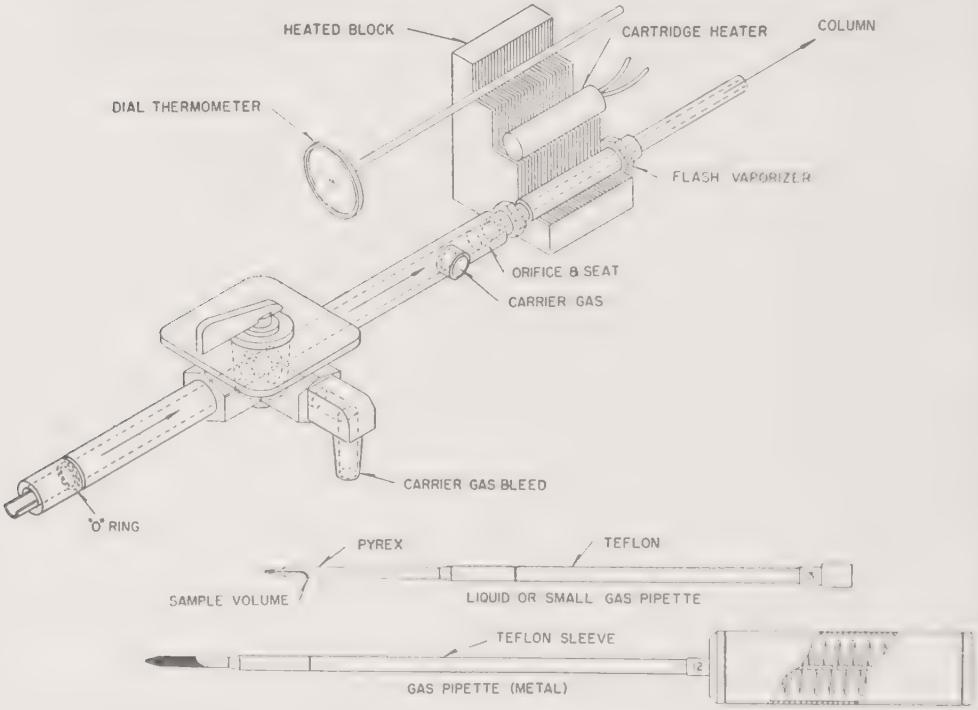


Fig. 3. Flash evaporator.

As the ambient cell temperature is increased the current input to the thermistors is increased to give nearly constant sensitivity.

While operating any except very special thermistors at high temperatures, the sensitivity is reduced because the resistance decreases. With an input of about 20 ma into the thermistors there is a very sharp decrease in sensitivity above 150°C.

We have not experienced a significant shortening of thermistor life as a result of exceeding the thermistor current rating for extended periods.

In working with high boiling materials there is a tendency for condensate or liquid phase to form in the cell when the cell temperature is much lower

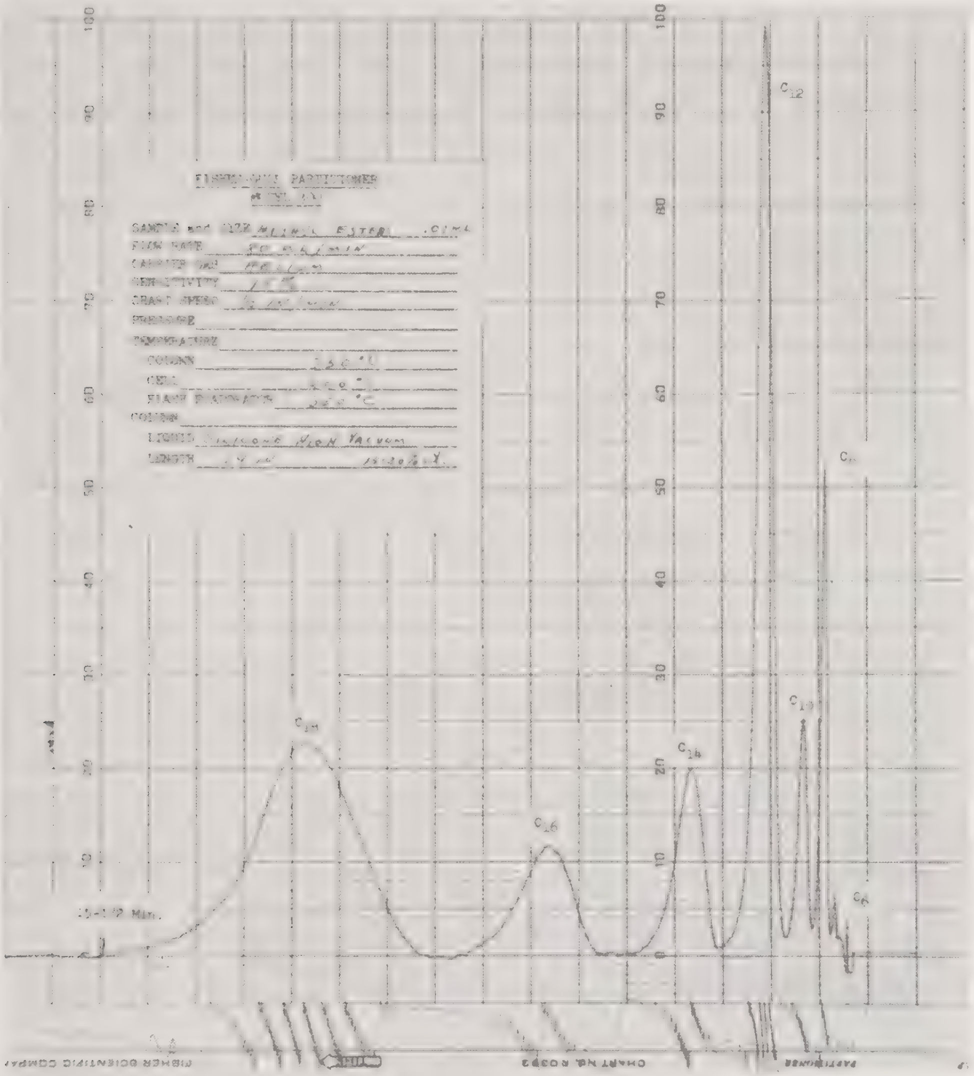
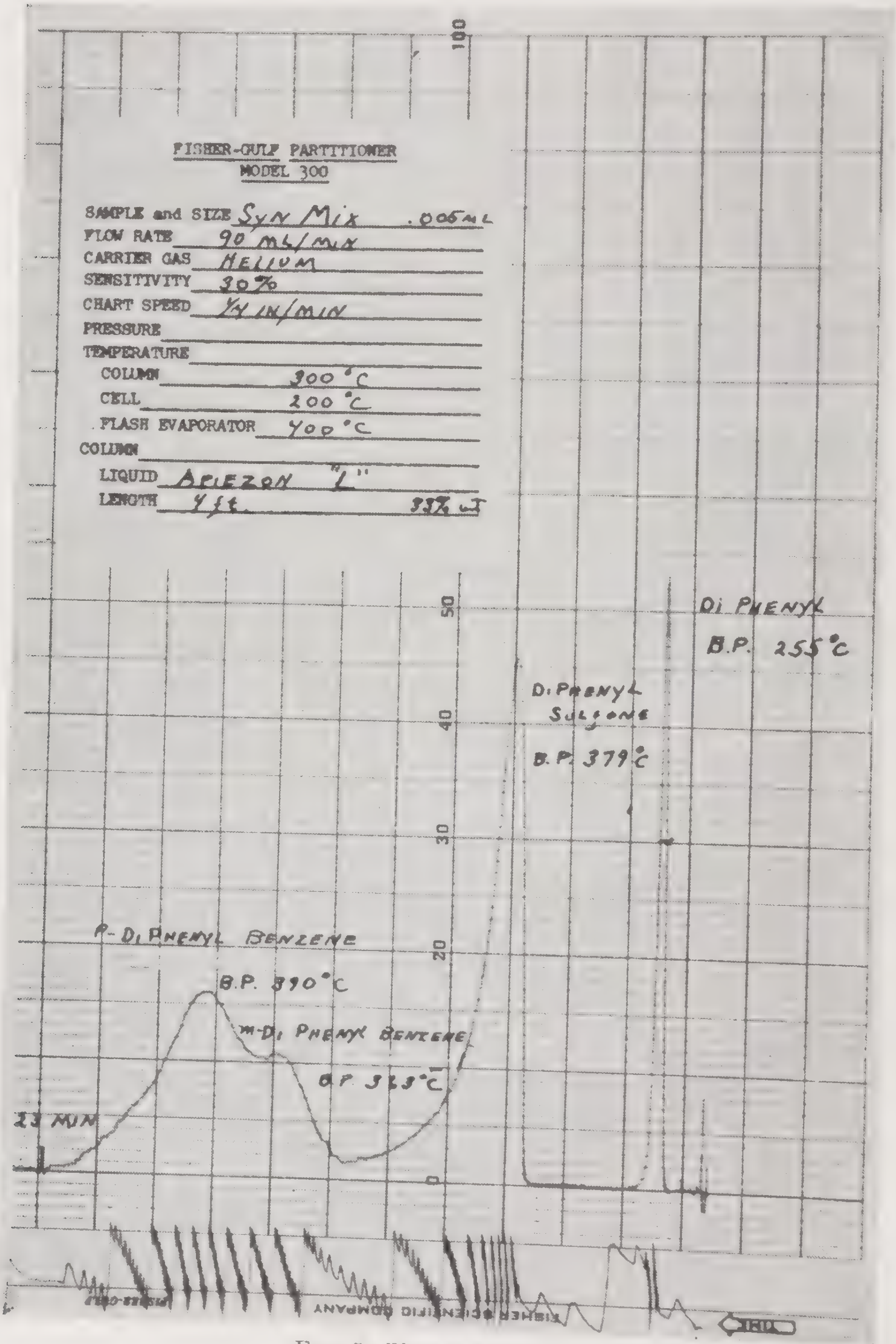


FIG. 4. Methyl esters.

than the column temperature. The cell is mounted in such a way that any liquid tends to drain out of the cavity housing the thermistor. Components with boiling temperatures of 400°C have not been a problem.

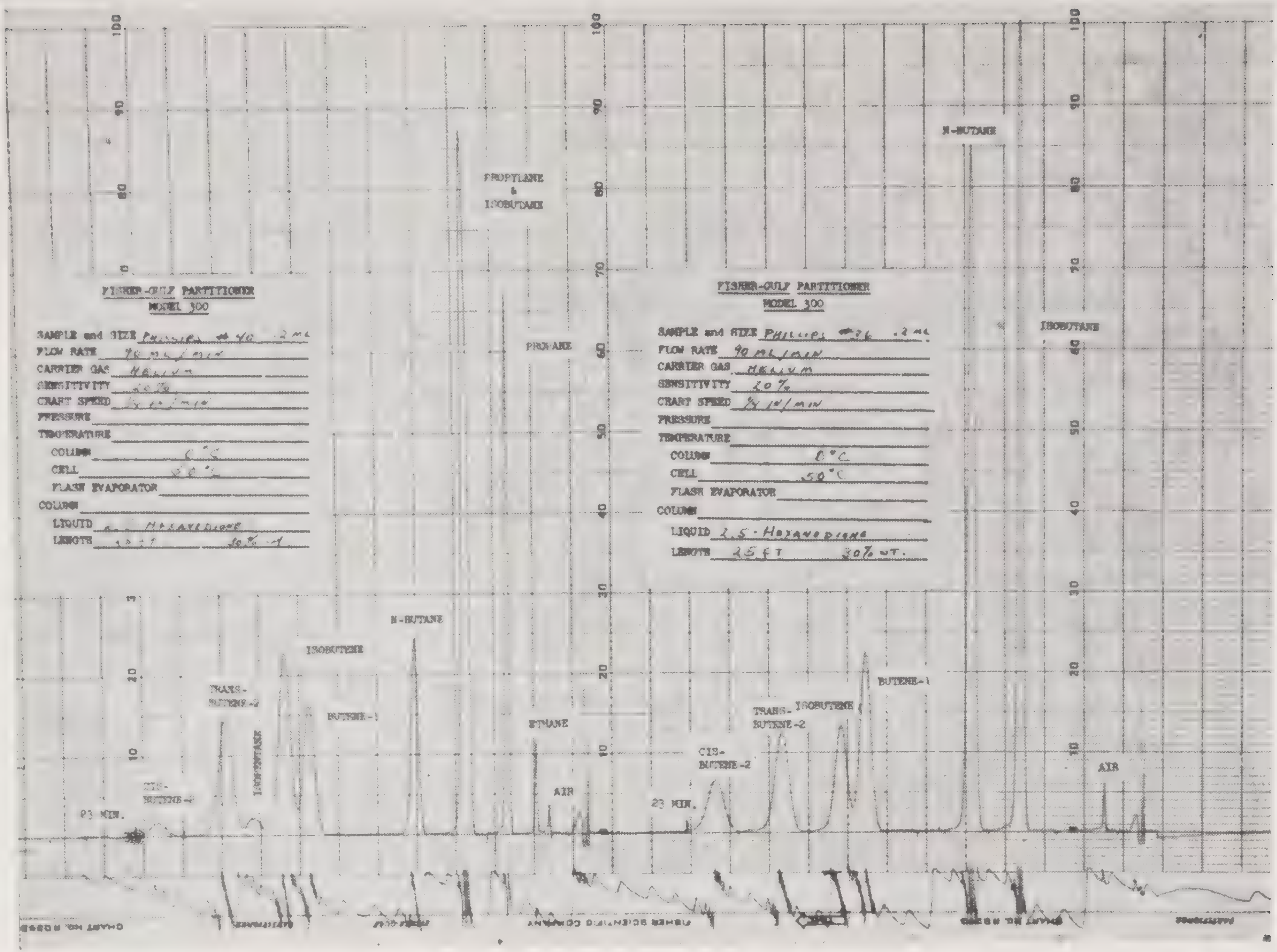
Actually, if the thermistor does pick up a small droplet of condensate



FISHER-GULF PARTITIONER
MODEL 300

SAMPLE and SIZE Syn Mix .005 ML
FLOW RATE 90 ML/MIN
CARRIER GAS HELIUM
SENSITIVITY 30%
CHART SPEED 1/4 IN/MIN
PRESSURE
TEMPERATURE
COLUMN 300 °C
CELL 200 °C
FLASH EVAPORATOR 400 °C
COLUMN
LIQUID APIEZON "L"
LENGTH 4 ft. 33% wt

FIG. 5. Phenyl benzene.



FISHER-GULF PARTITIONER
MODEL 300

SAMPLE and SIZE Phillips #40 .2 ml
FLOW RATE
CARRIER GAS Helium
SENSITIVITY
CHART SPEED
PRESSURE
TEMPERATURE
COLUMN
CELL
FLASH EVAPORATOR
COLUMN
LIQUID
LENGTH

FISHER-GULF PARTITIONER
MODEL 300

SAMPLE and SIZE Phillips #36 .2 ml
FLOW RATE 90 ml/min
CARRIER GAS Helium
SENSITIVITY 20%
CHART SPEED ½ in/min
PRESSURE
TEMPERATURE
COLUMN 0°C
CELL 50°C
FLASH EVAPORATOR
COLUMN
LIQUID 2,5-Hexanedione
LENGTH 25 ft 30% wt.

FIG. 6. Analysis of isobutylene and butene-1.

(evidenced by very erratic recorder behavior), it can most often be dislodged by a solvent.

Automatic integration of the area under the curve has been widely accepted. However, with the pip type trace which we employ, it is difficult

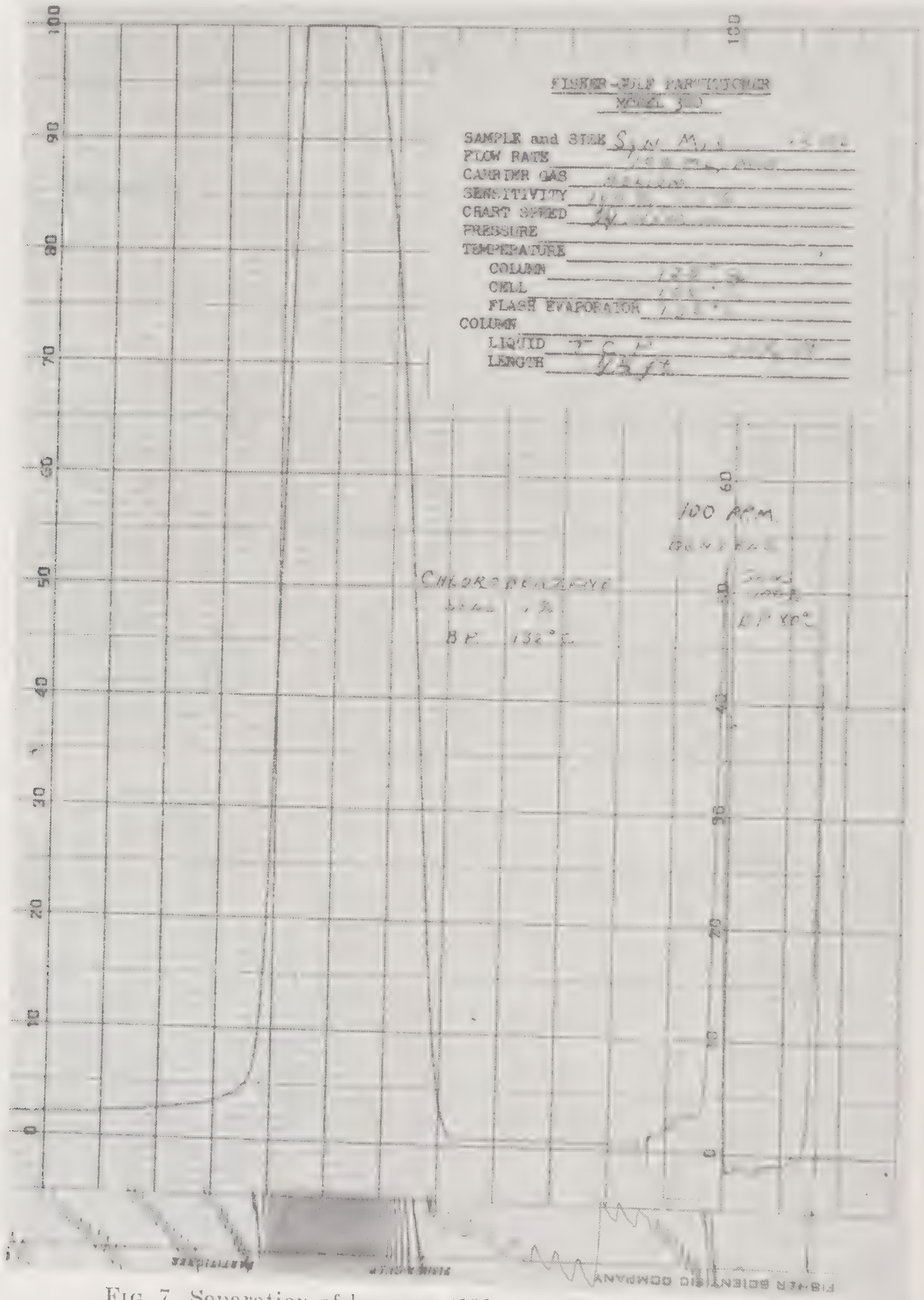


FIG. 7. Separation of benzene (100 ppm) from chlorobenzene.

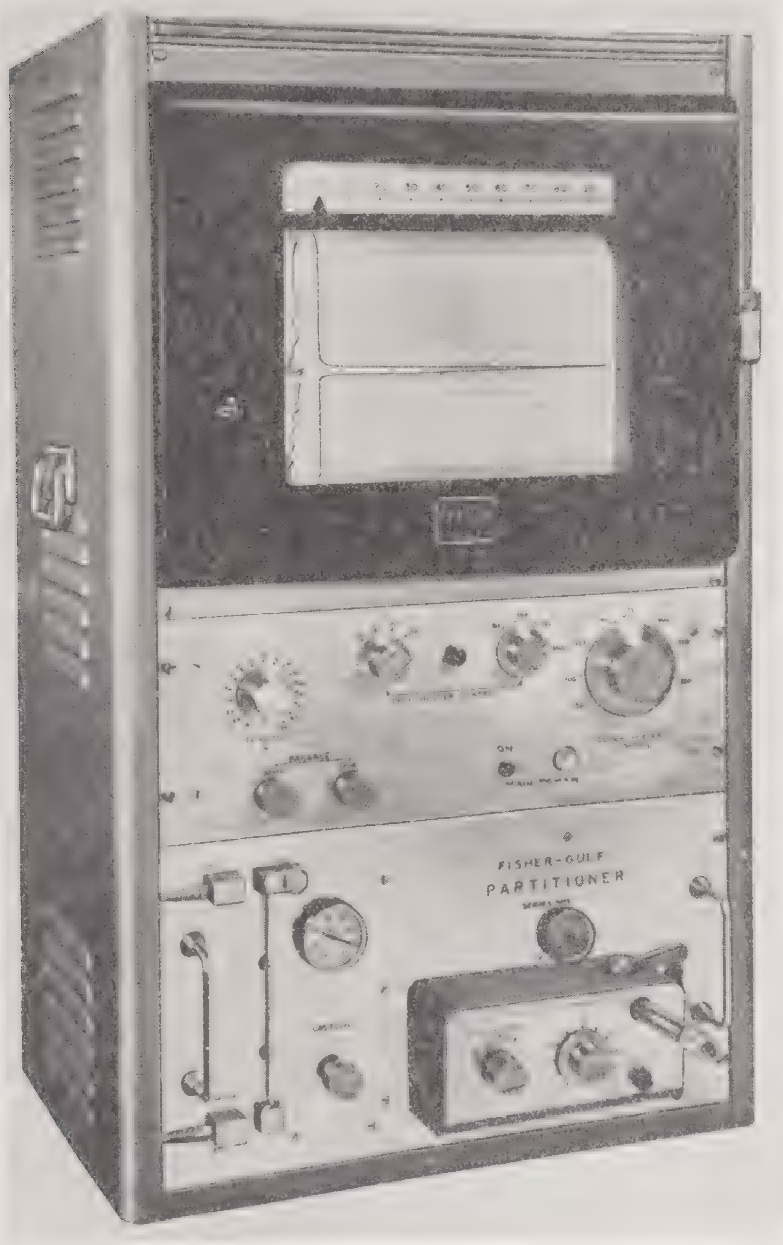


Fig. 8. Instrument.

to count the pips accurately at full scale deflection. A method of making a novel trace has been developed making it possible to count the pips more accurately. With the new trace it is possible to increase the integrator disc drive speed, thus increasing the number of pips per unit time.

There are many difficulties encountered in high temperature gas chromatography. Getting the sample into the system and vaporized quickly, and maintaining good sensitivity, are certainly real problems.

Probably the most difficult one, however, is to find a liquid phase which will separate the sample into its various components and, in addition, "stay put" on the column. Here is a list of materials we have uncovered or heard about, which have proven moderately satisfactory.

1. Apiezon Grease "L"
2. D.C. Silicone High Vacuum Grease (Extracted with ethyl acetate)
3. Stearone
4. Polyethylene
5. Aromatic Extracts

Employing a few of the above liquid phases as packing we have carried out some separations of high boilers that indicate the type of results obtained at different temperature conditions. These are shown in Figs. 4 and 5.

The analysis of isobutylene and butene-1 has always been somewhat of a problem. Figure 6 shows this separation operating the instrument at 0°C. Analysis has also been carried out by changing the column temperature during an analysis.

Figure 7 is an example of the sensitivity that can be expected with this instrument in separating benzene from chlorobenzene.

A formal picture of the instrument is shown in Fig. 8.

Designing an instrument to overcome some of the mechanical and thermal problems has been a real challenge. The application of a high temperature unit to the analysis of high boilers surely presents an equal one.

The satisfactory routine analysis of such things as fatty acids, high molecular weight hydrocarbons, ketones, alcohols, etc., is sure to come in time with the introduction of high temperature gas chromatography apparatus. Great possibilities are evident in the clinical field. The use of reduced pressures in combination with high temperature certainly broadens the scope of application even more.

Discussion

Knoblauch (*Minneapolis-Honeywell Regulator Co., Pennsylvania*): What is the maximum pipping rate of your integrator?

Taylor: We have an input motor giving us an input of 8 rpm on a mechanical integrator with an output at full scale deflection of about 200 pips per minute.

Knoblauch: Based on previous questions in earlier sessions, 200 pips per minute seems to be on the slow side. I am wondering about your experience.

Taylor: I would definitely state that the more counts per minute that one can get, the more accurate the results will be.

CHAPTER XVIII

The Selection and Operation of Thermistors for Katharometers

C. B. COWAN AND P. H. STIRLING

Central Research Laboratory, Canadian Industries Limited
McMasterville, Quebec

The thermal conductivity cell or katharometer is a well established instrument for the detection of changes in gas composition. The katharometer is one of the simplest detectors available; it is cheap, robust, and reliable, and as a result of these characteristics it is the detector most widely utilized in gas chromatography units today. Renewed attention has therefore been recently directed towards the parameters which should be considered in the design of a thermal conductivity cell.

One must ask oneself what is required of a thermal element for use in a thermal conductivity cell, and one might then prepare a list as follows.

A thermal element should have the following properties.

1. A large output for normal changes in conductivity such that the ordinary 0 to 10 mv recorder may be used directly.
2. A high sensitivity coupled with a low noise value so that the signal would be suitable for electronic amplification.
3. Reproducibility and stability.
4. Identical and interchangeable units must be readily available.
5. Reasonable power supply requirements.
6. Be capable of operation over a wide range of temperature.
7. Chemical inertness.
8. A time constant not greater than 5–10 seconds.

The selection of a detecting element for use in a katharometer must of necessity involve several compromises, and it is our purpose to clarify the factors involved so that a clear cut decision may be arrived at for any particular application. Perhaps the most important single requirement is that the sensing element itself should exhibit a large change of resistance with temperature, and from this point of view thermistors are particularly attractive. However, despite the widespread use of thermistors in thermal conductivity cells very little appears to have been published on the actual selection of a thermistor for use in a particular katharometer or on the choice of optimum operating conditions.

Anyone wishing to use a katharometer containing thermistors has two alternatives, either he buys a complete commercial detector or he builds his own. In the former case he has to rely on the manufacturer's experience to choose the best thermistor and to recommend the correct operating conditions. Unthinking adherence to the manufacturer's general recommendations may not always yield the maximum sensitivity, as is shown in Figs. 1 and 2. These are plots of the sensitivity of a thermistor katharometer expressed as peak height in scale divisions for a given change of composition versus the voltage applied to the bridge. The two curves in Fig. 1 refer to different components in nitrogen as the carrier gas. The operating voltage recommended (3.5 volts) is not far removed from the maximum sensitivity attainable with nitrogen.

On changing the carrier gas to hydrogen a somewhat different state of affairs results. Figure 2 shows the peak height in mm versus the bridge voltage for two components in hydrogen as the carrier gas. Here one can see that the recommended voltage places one on the other side of the maxima and at about one-sixth of the maximum value of sensitivity. It is thus necessary to ascertain the best operating conditions for each carrier gas for a given cell.

If one wishes to construct one's own detector one is faced with a bewildering array of shapes, sizes, resistance values, lead materials, and resistance temperature characteristics. Figure 3 shows some of the thermistors used in our experiments; they differ in size, shape, and surface to volume ratio.

The thermistor also possesses other properties which may be confusing.

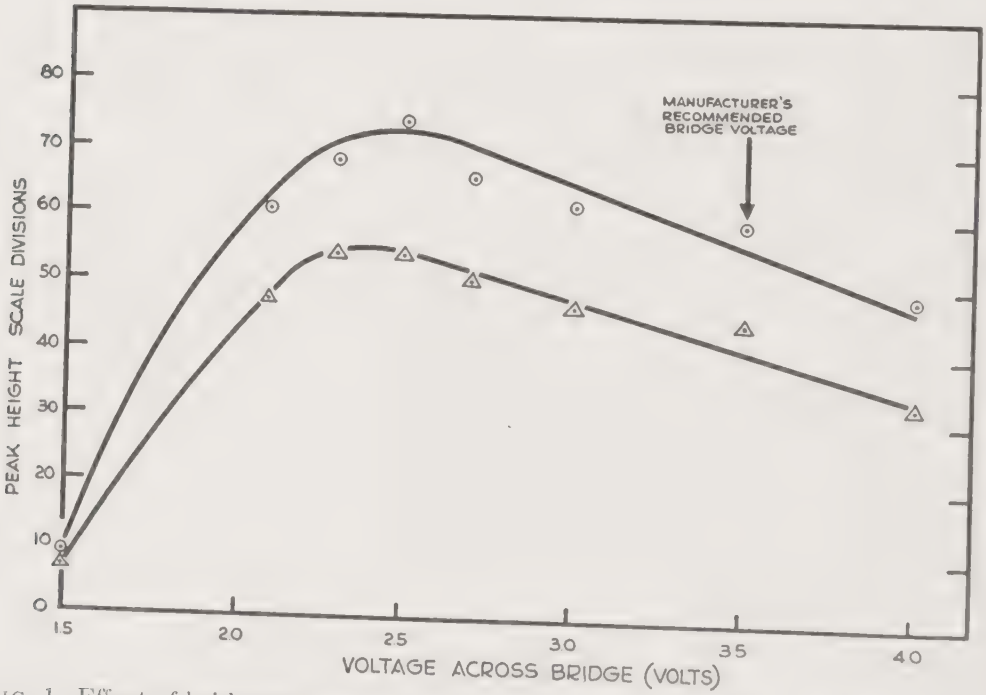


FIG. 1. Effect of bridge voltage on sensitivity. Carrier gas nitrogen, 35 ml/minute.

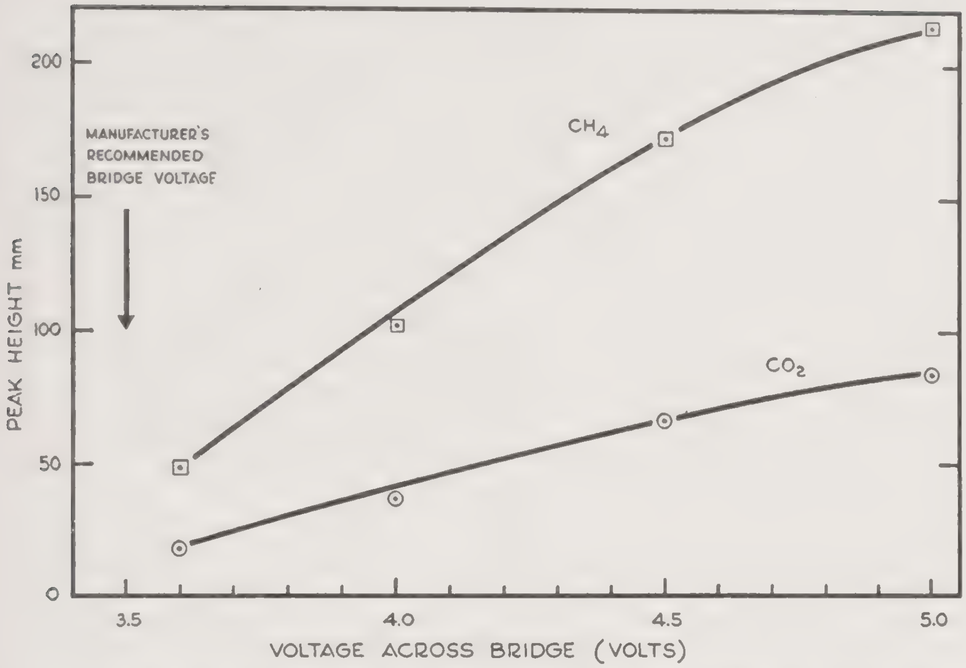


FIG. 2. Effect of bridge voltage on sensitivity. Carrier gas hydrogen, 105 ml/minute.

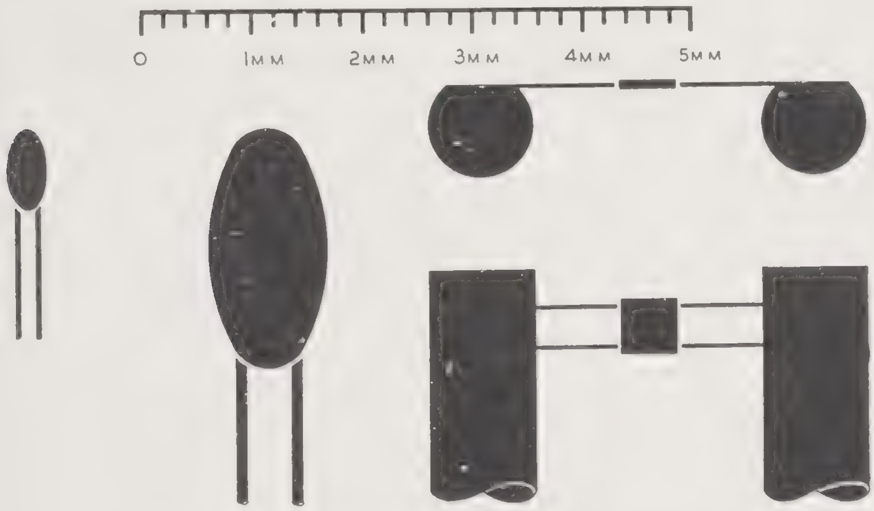


FIG. 3. Thermistors used in sensitivity measurements.

It can have the same resistance at two values of current and it can easily destroy itself by thermal overloading; therefore the bridge circuit used in conjunction with thermistors must be carefully chosen.

There are many possible bridge arrangements but for use with thermistors the parallel fed bridge, Fig. 4, is preferable to the series type, Fig. 5, since it can be more easily designed to prevent thermal runaways. In our experiments we adopted the usual form of bridge with four equal arms, and the out-of-balance signal was displayed on a recorder of suitable range. In order to simplify the experimental work, a single active bridge arm was used in the sensitivity measurements, as shown in Fig. 6. The experimental arrangement of the gas flow system was quite conventional, (Fig. 6) and a diffusion type cell (Fig. 8) similar to a commercially available unit was employed.

The relative sensitivity versus current for a thermistor katharometer is shown in Fig. 9. The current through the thermistor has a profound influence on the sensitivity of the katharometer and this dependence is dif-

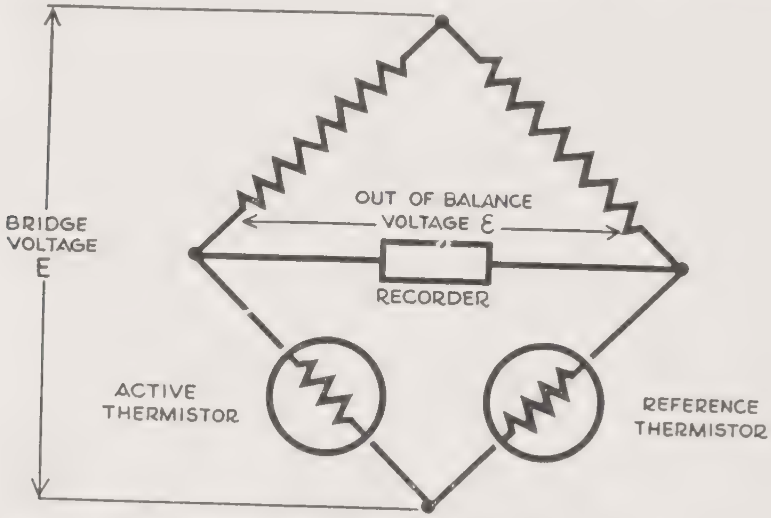


FIG. 4. Parallel fed thermistor bridge (preferred arrangement).

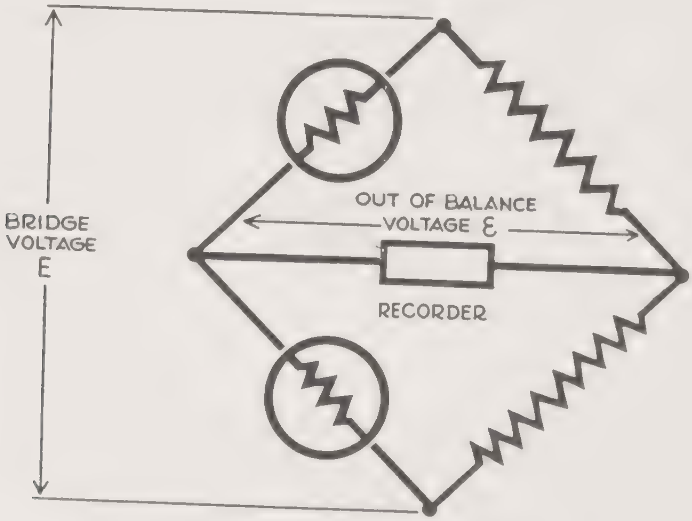


FIG. 5. Series fed thermistor bridge.

ferent from that shown by the more familiar hot wire katharometer, the shape of which is indicated by the dotted line.

It can be seen that a maxima exists in the case of the thermistor katharometer. The "sensitivity" in these experiments was expressed as the millivolts output from an equal arm bridge for a given composition change, which was from nitrogen to 1.3% CO_2 in nitrogen.

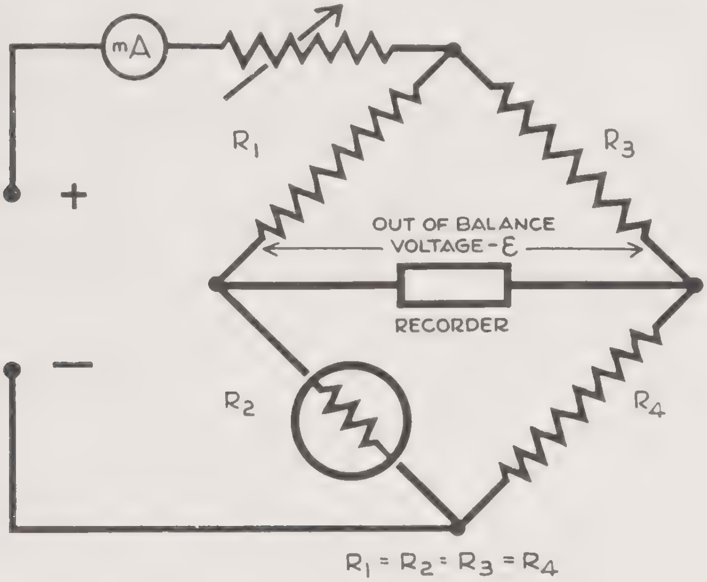


FIG. 6. Experimental bridge arrangement.

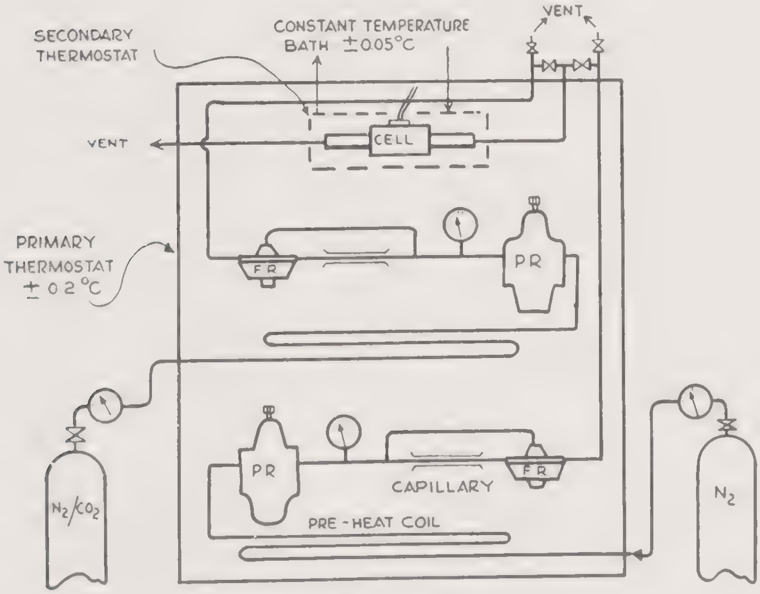


FIG. 7. Gas system.

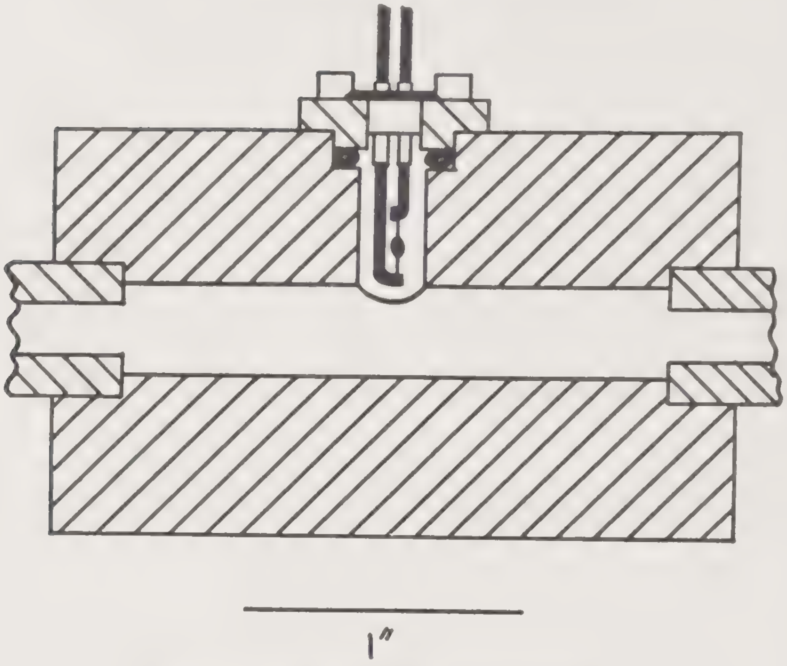


FIG. 8. Experimental katharometer.

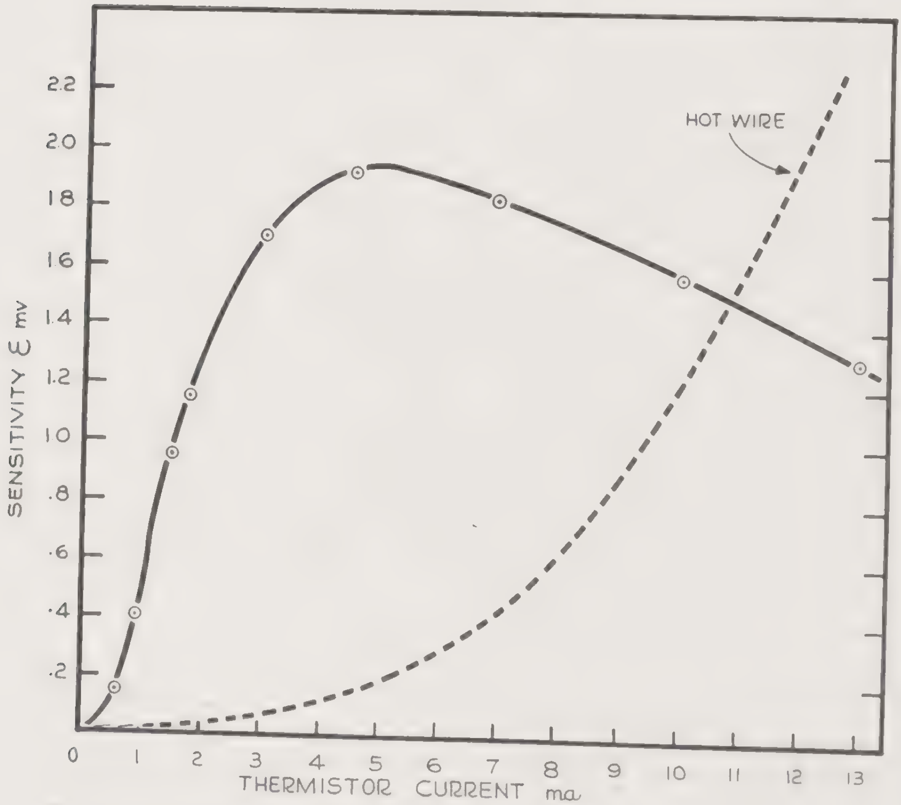


FIG. 9. Mv output for N_2 vs. 1.3% CO_2 in N_2. R_{25} = 2000 ohms.

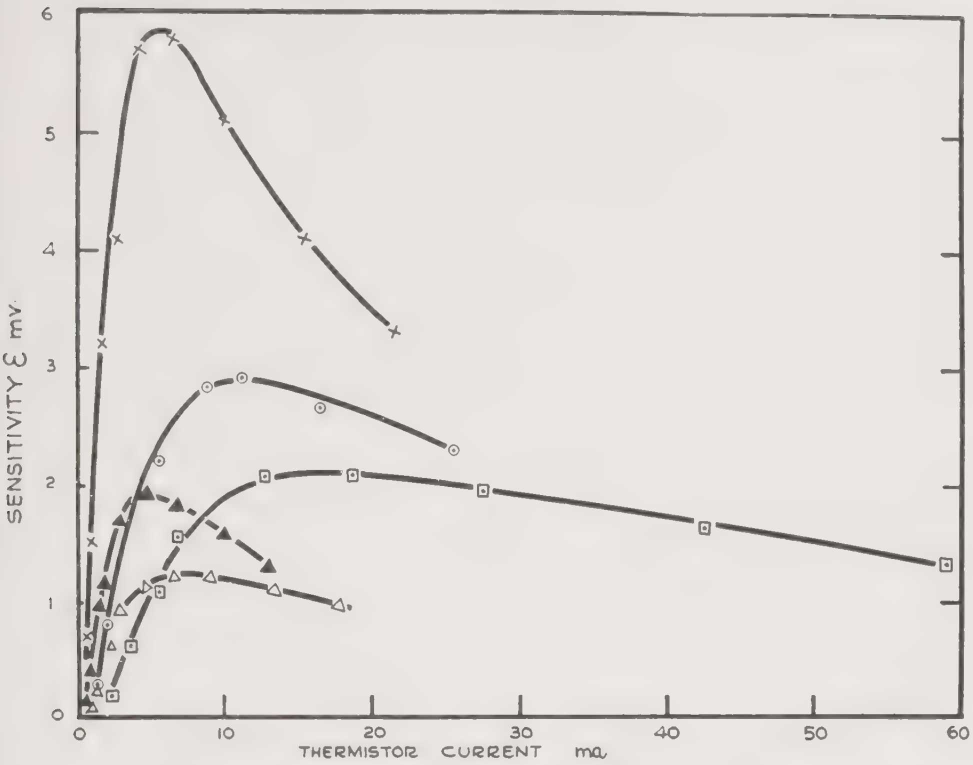


FIG. 10. Sensitivity versus current. Key: × = 8670 ohms; ⊙ = 1760 ohms, ▲ = 2350 ohms; ⊡ = 1010 ohms; △ = 1080 ohms.

The temperature difference (θ) between the thermistor and the cell wall is a more useful and representative parameter than the bridged current or voltage which is commonly used. This point is illustrated in Fig. 10 and 11

Figure 10 is a somewhat confused plot which shows sensitivity versus thermistor current for several thermistors of various sizes, shapes, and resistances; it can be seen that the maxima appear at various thermistor currents. On changing the abscissa from thermistor current to temperature difference (θ) in °C, Fig. 11, an orderly series of curves is obtained from the same data. The maxima are now almost superimposed and correspond to a temperature difference somewhere between 50 and 70°C.

It may be seen that in general the larger the resistance the greater the sensitivity. Resistance alone is not the determining factor as can be seen by comparing the curves for the 1,000 ohm thermistors which are quite different in magnitude. (The steepness of the high resistance curves is due to a scale factor as can be seen by comparing the curves for the 8,000 ohm thermistor bead which is the highest curve in Fig. 11 and the lowest curve in Fig. 12. The sensitivity scale on Fig. 12 has been compressed about fourfold compared to that on Fig. 11. If one compares the curves for the 130,000 ohm and the 127,000 ohm thermistors one again sees a disparity in magni-

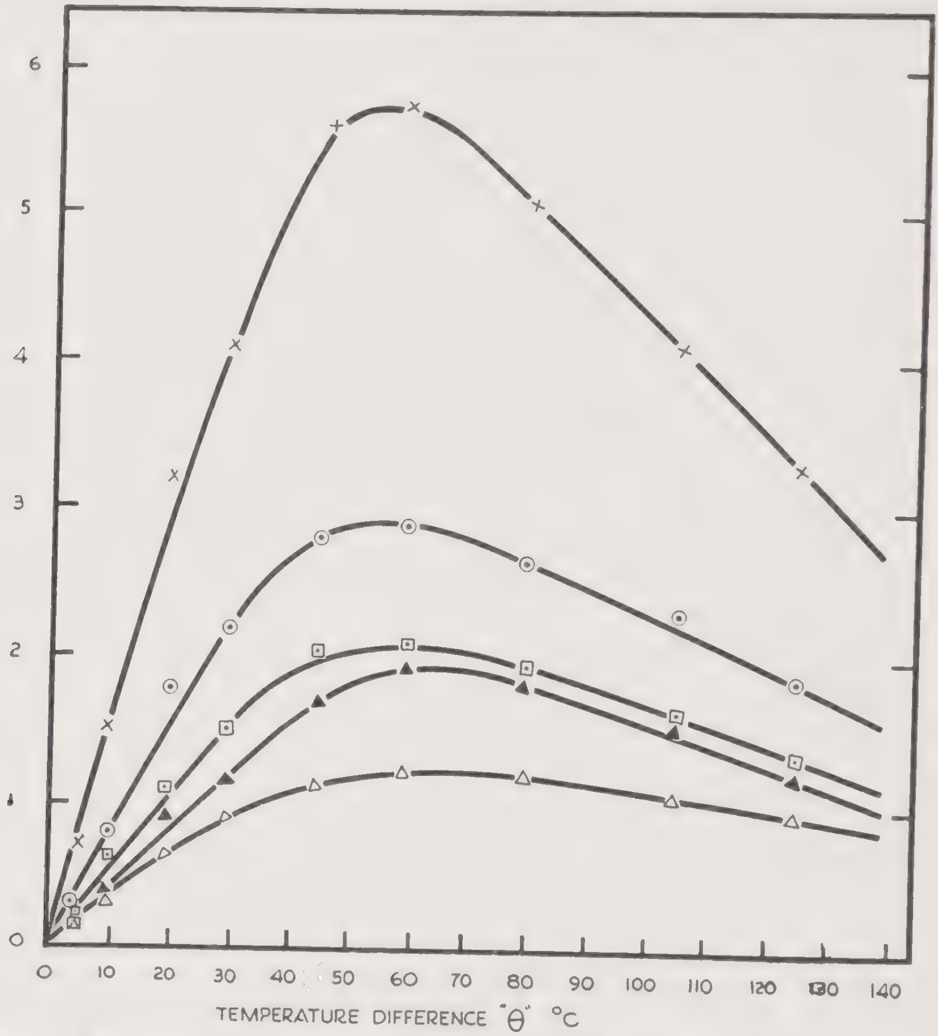


FIG. 11. Sensitivity versus temperature difference. Key: × = 8670 ohms; ⊙ = 1760 ohms; ⊡ = 1010 ohms; ▲ = 2350 ohms; △ = 1080 ohms.

tude although the maxima in these curves all lie fairly close to a temperature difference (θ) of 50°C.

The other factor that must be taken into account is the dissipation constant, which is affected by the size and shape of the thermistor; thus in general a bead of large surface area has a correspondly large dissipation constant. The dissipation constant is normally expressed as the milliwatts required to raise the thermistor temperature 1°C in still air, but the dissipation constants used in Fig. 13 were obtained by dividing the power dissipated in raising the thermistor bead 50°C in the flowing gas stream by fifty. In general the dissipation constants so obtained were lower than the manufacturer's quoted values.

Figure 13 shows a plot of the sensitivities expressed as in millivolts out-

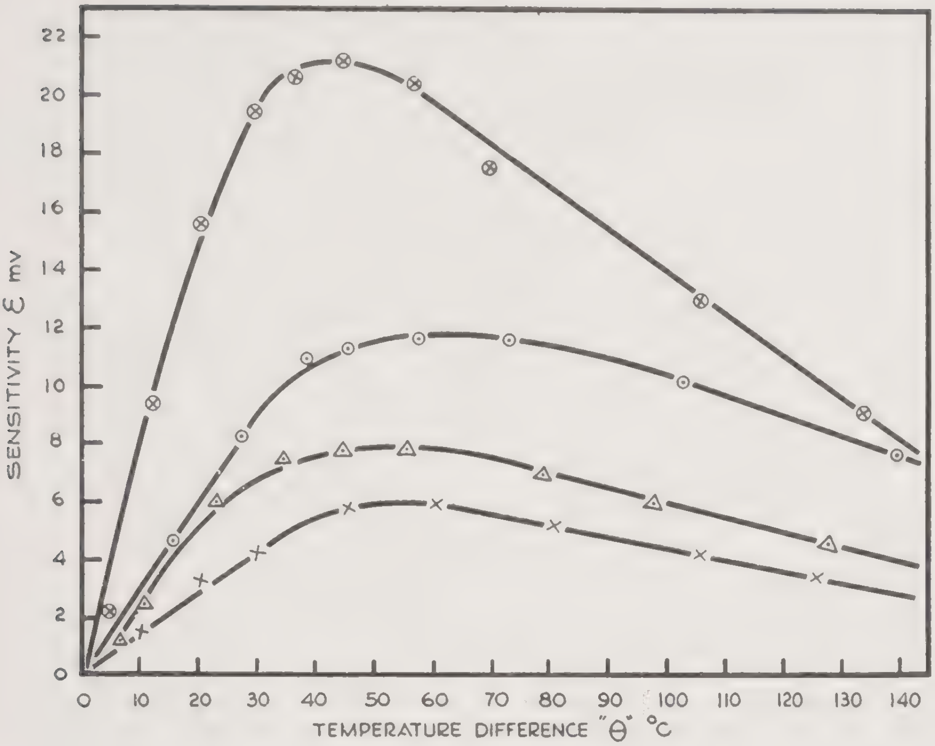


FIG. 12. Sensitivity versus temperature difference. Key: ⊗ = 130,000 ohms; ⊙ = 127,000 ohms; △ = 57,200 ohms; × = 8670 ohms.

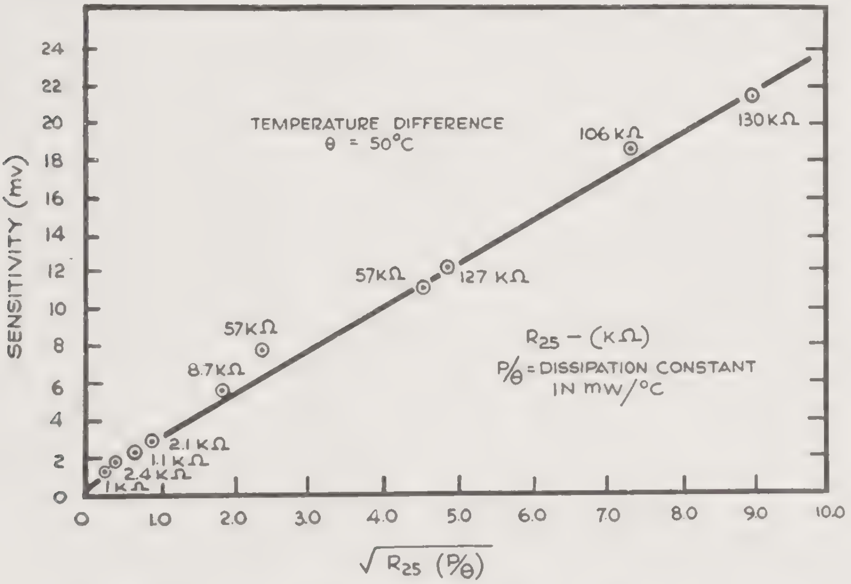


FIG. 13. Sensitivity versus $\sqrt{R_{25}(P/\theta)}$ for various thermistors.

put for a change in composition from nitrogen to 1.3% CO_2 in nitrogen for a single value of temperature difference $\theta = 50°C$ versus the square root of the product of the resistance at 25°C times the dissipation constant. An almost linear relationship is obtained in spite of the differing sizes, shapes, materials of construction, sources of supply (thermistors from four manufacturers were used), and wide range of resistances covered.

This plot immediately shows that the highest usable value of the term $\sqrt{R_{25}P}/\theta$ is desired for maximum sensitivity to be attained. However, one must inevitably compromise. A large value of the dissipation constant is accompanied by a long time constant, and a large value of resistance makes the design or choice of an out-of-balance recorder difficult.

If one uses a diffusion type of cell the overall time constant is usually about 5 to 10 seconds, and thus there is no point in choosing a thermistor with a very short time constant or one with a time constant greater than 10 seconds. The physical form of the cell can thus be used to deduce the acceptable limits of the dissipation constant.

The choice of the recorder likewise fixes the maximum thermistor resistance that can usefully be employed in a Wheatstone bridge, since if the recorder input resistance is lower than the resistance of the bridge arm a loss of sensitivity occurs. Recorders are available which have input resistances of 30,000 ohms so that thermistors of high resistance can be used and a high sensitivity achieved. Thus, under our experimental conditions a tenfold increase in sensitivity could be achieved by changing the thermistor resistance from 1,000–100,000 ohms, and at the same time substituting in the millivolt recorder a servo-amplifier with an input resistance of 7,000 ohms for the common unit which has an input resistance of about 400 ohms .

If despite these increases in sensitivity one is still faced with a small signal then electronic amplification must be considered. A stable base line or bridge balance is necessary, and for this purpose accurately matched pairs of thermistors must be obtained. The matching of pairs of thermistors to compensate for temperature and bridge supply voltage changes involves the matching to within specified tolerances of three things: (*i*) resistance values, usually at 25°C, (*ii*) the percentage change of resistance with temperature, (*iii*) the dissipation constants. These are stringent requirements and the appendix shows how permissible tolerances may be calculated if the voltage and temperature regulation are known.

The signal to noise ratio is the next item to be considered. The most troublesome noise frequencies, that is, those which have the greatest effect on normal chopper amplifiers and recorders, lie in the low frequency range from .01 to 200 cycles per second. Noise was measured with several band widths, and center frequencies of 3 cycles a second and 7 cycles a second were used chiefly. The experimental arrangement for the measurement of electrical noise is shown in Fig. 14. The apparatus was double-screened and a special ground was employed. The basic noise level of the apparatus was kept down to 1–1.5 microvolts in the 1 MΩ input resistor of the band pass amplifier. The resistance of the thermistor at a particular current level was obtained by measuring the voltage across it by means of a V.T.V.M. which was disconnected during noise measurements. All connections were soldered and frequent checks of the basic noise level were made by soldering in a precision wire-wound manganin resistor in place of the thermistor. The presence of 60 cycle pickup was tested for by always observing the noise levels obtained in the 0.5–50 c/s and 0.2–250 c/s bands. (The frequencies are the −3 db points). If the ratio of the latter to the former increased then 60 cycle pickup was suspected and remedial action would be taken. Experiments were conducted at night and at such times as other electrical apparatus in the laboratory was not operating to minimize external interference.

Noise in semi-conductors depends upon a myriad of factors: resistance, current, temperature, voltage-gradient, size, shape, and past history, and we cannot undertake to consider all of these factors, or indeed any of them in great detail. A few general remarks can be made and these are illustrated by the following figures. The curves of noise measurements refer to an individual thermistor with a definite history, and as variations occur from thermistor to thermistor these should only be considered as a general in-

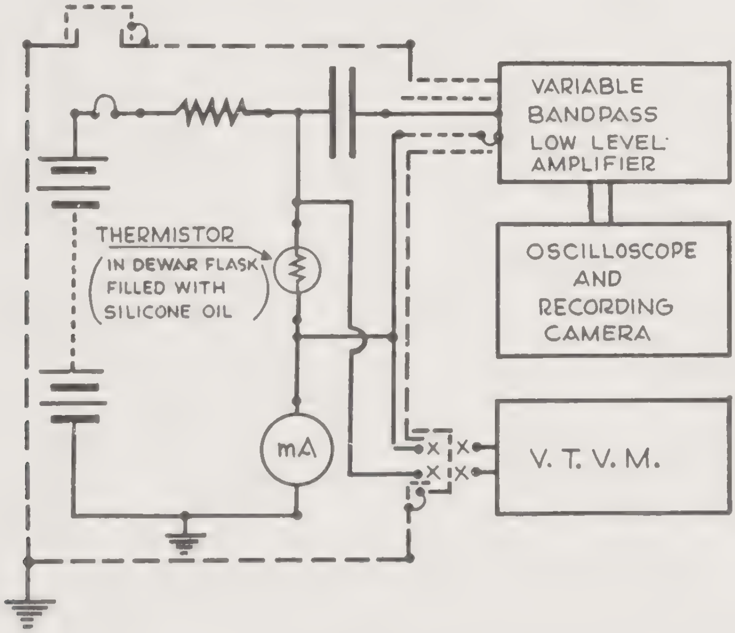

VARIABLE BANDPASS LOW LEVEL AMPLIFIER
OSCILLOSCOPE AND RECORDING CAMERA
THERMISTOR
IN DEWAR FLASK FILLED WITH SILICONE OIL
mA
V. T. V. M.

FIG. 14. Experimental arrangement for noise measurements on thermistors.

dication of the behavior to be expected. Our remarks should not be taken as implying that thermistors are superior to hot wire katharometers for handling low signals as many other factors must be taken into consideration.

Rapid temperature fluctuations due to microturbulence, variations in flow, inlet gas temperature, and bridge supply voltage changes make *electrical noise* measurements difficult and our experimenst were therefore designed to minimize these temperature effects. Thus after we had satisfied ourselves that the noise level obtained in silicone oil at low current levels was close to that obtained with the same thermistor in air, we used oil as the ambient medium for the remaining experiments. Since noise is dependent on the resistance in which it occurs the noise is expressed as microvolts per thousand ohms in order to separate out various effects.

Figure 15 shows the dependence of electrical noise in microvolts per thousand ohms for various thermistors as a function of the current in milliamps. In general the larger the physical size of a thermistor the higher the noise level. Furthermore, high resistance materials tend to be noisier than low resistance materials. It can also be seen that electrical noise is very dependent on current and in our experiments the exponent n in the relationship; Noise $\propto I^n$, was found to range from 1.2 to 1.8.

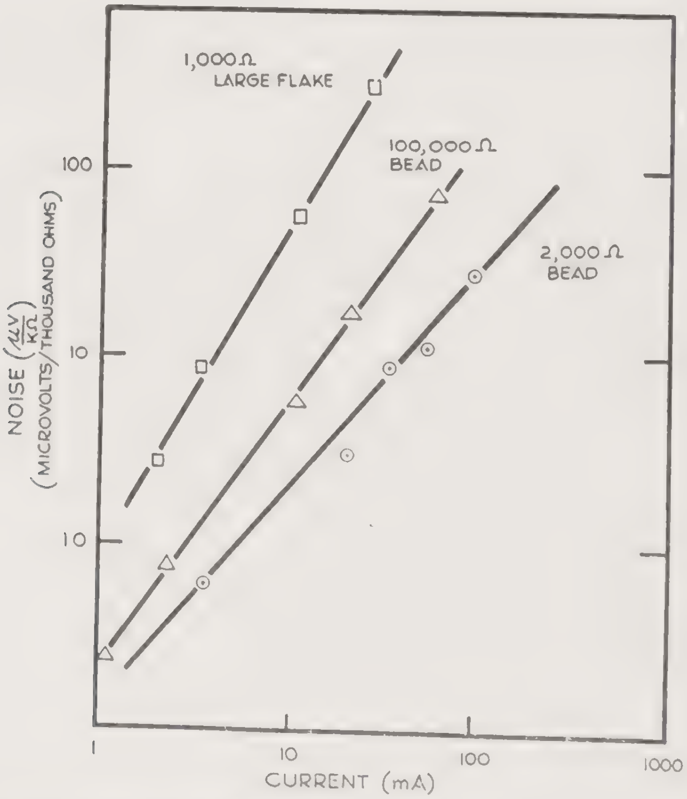


FIG. 15. Noise in thermistors (immersed in silicon oil at 30°C).

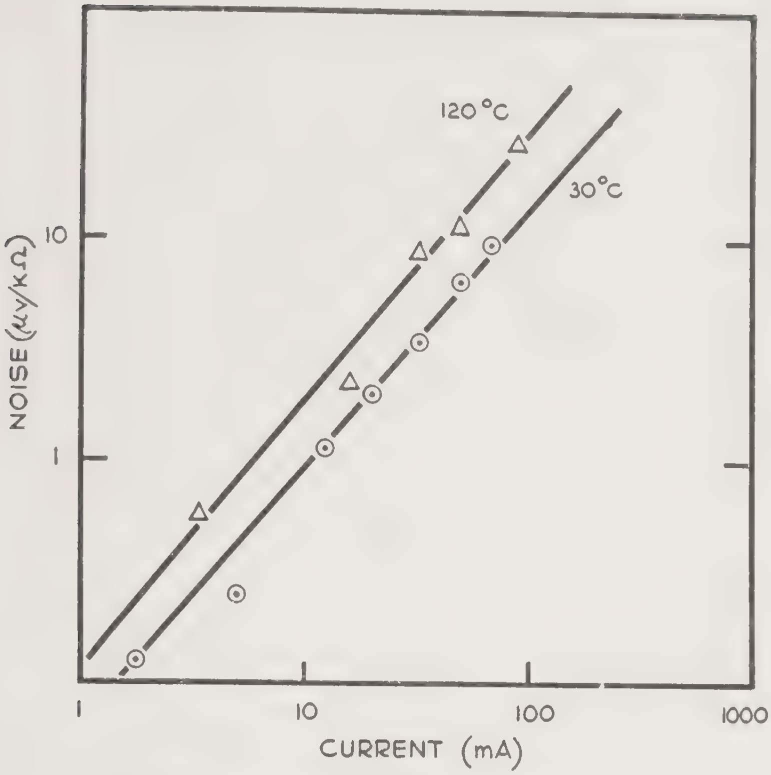


FIG. 16. Effect of temperature on noise (2000 ohm bead).

The effect of temperature was ascertained in a series of experiments by immersing a thermistor in preheated oil contained in a Dewar flask. Theoretically the noise should increase with temperature and this was found to be the case with well-aged thermistors (Fig. 16). The effect of temperature on noise in new thermistors was not reproducible and showed marked hysteresis effects (Fig. 17).

Since aging appears to be a function of a particular batch of thermistor material, no definite procedure for obtaining a correctly aged thermistor can be given. Thermistors can be aged in two ways, either by heating in an oven to a temperature higher than that at which they will be operated for several hours, or by passing current through them which heats them to a resonable temperature. During this aging process small changes in resistance and resistance-temperature coefficients may occur so that matching procedures should preferably be carried out after aging. The noise level slowly decreases over a period of time when a steady current is passed through a thermistor. Figure 18 shows that it is advantageous to keep the current on continuously and to avoid even short interruptions of current in critical applications so as to minimize the electrical noise level.

The electrical noise, katharometer sensitivity, and the signal to noise

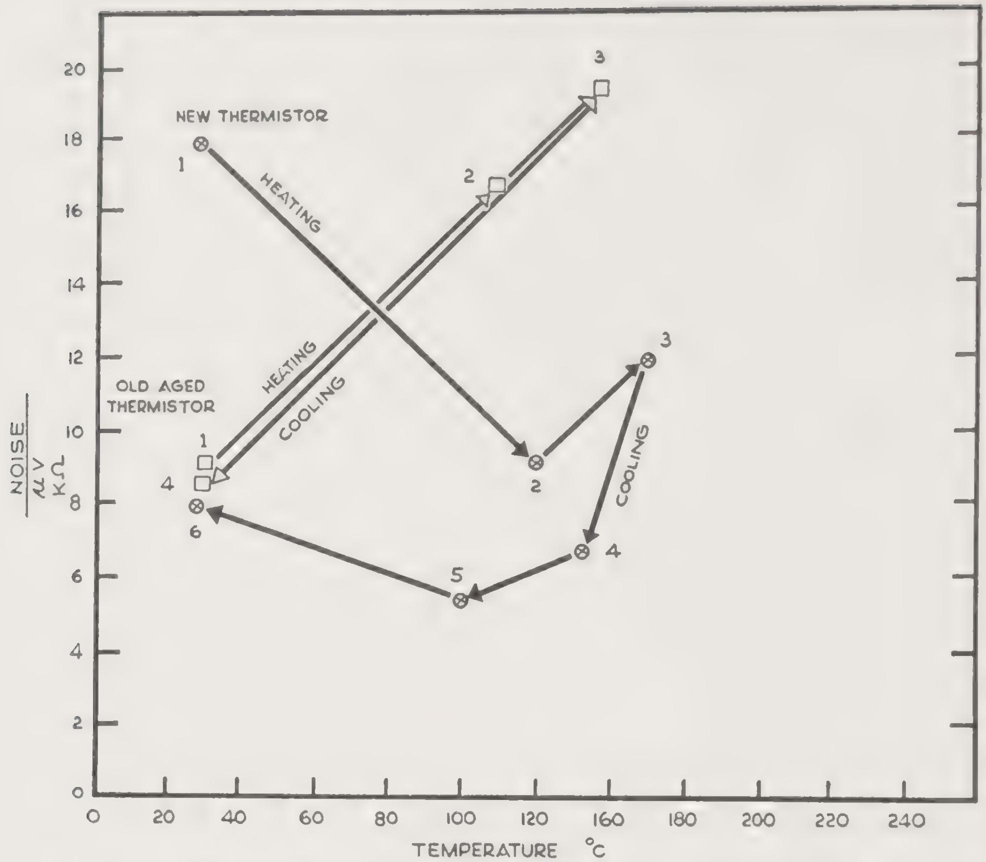


FIG. 17. Hysteresis effects in noise from new and aged thermistors on heating and cooling in oil at a fixed current.

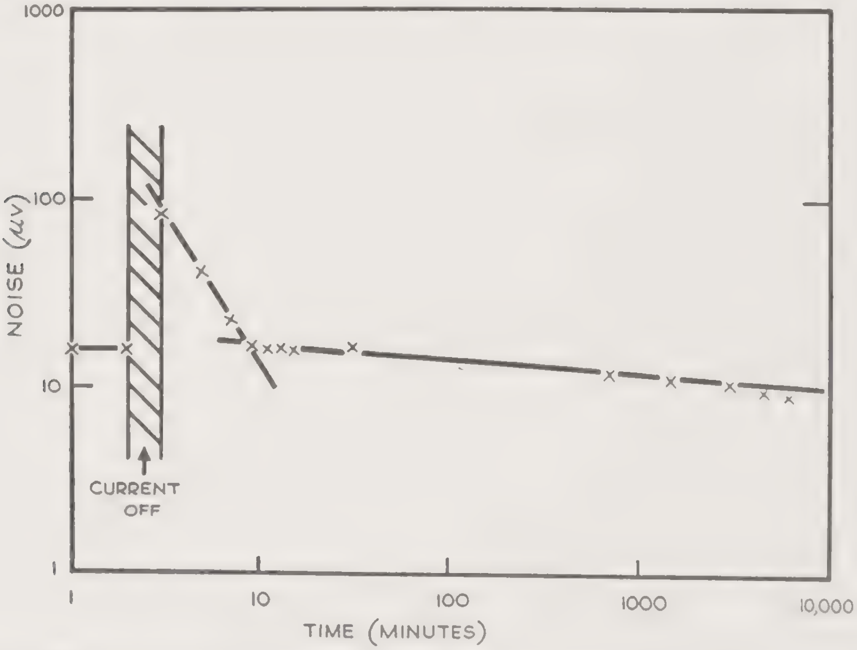


FIG. 18. Noise changes on interrupting thermistor current (17 mA, 2000 ohm bead)

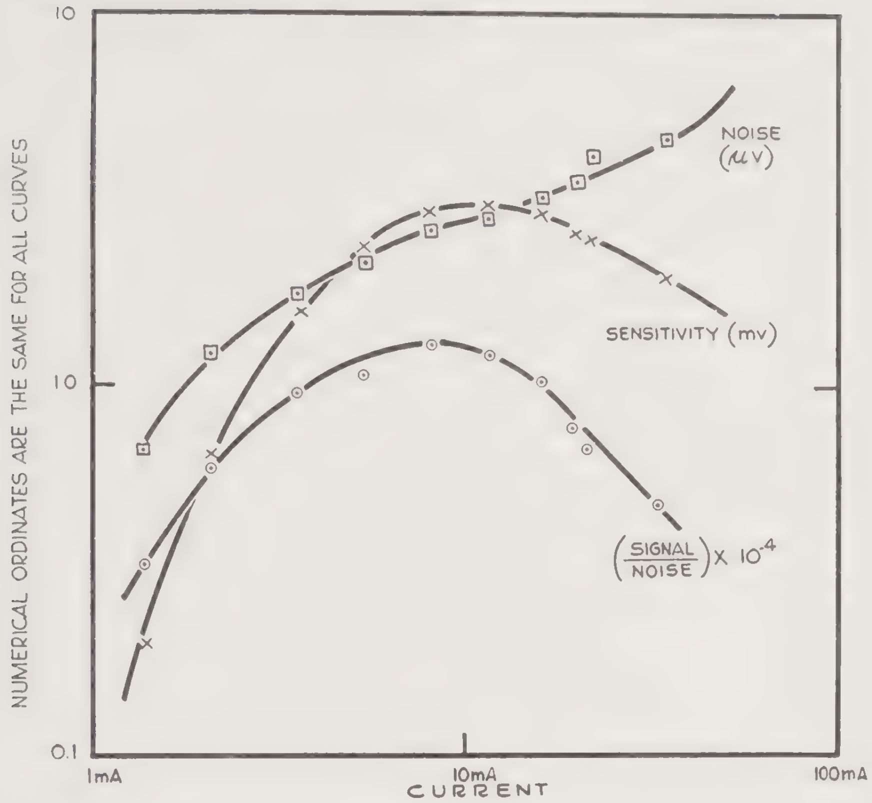


FIG. 19. Sensitivity noise and signal noise ratio (2000 ohm bead thermistor).

ratio for one thermistor are shown in Fig. 19. The noise level is expressed as straight microvolts not as microvolts per thousand ohms. The same ordinates are used for each quantity and the scale factors are indicated on each curve. The maxima of the signal to noise ratio curve is displaced, occurring at a lower value of current and hence a lower temperature difference than the maxima for the sensitivity curve. It can be seen that in order to obtain the highest values of the signal to noise ratio with thermistors it is essential to operate at relatively low currents and correspondingly low temperature differences, (about 40–60°C) and to minimize the other noise contributors such as variations in bridge-supply voltage, thermostat temperature fluctuations, or flow noise.

A further reason for operating at relatively low temperatures with thermistors is illustrated in Fig. 20 which shows the effect of cell block temperature on the sensitivity. The sensitivity falls off with increasing cell block temperature and in general thermistors are best suited for low temperature operation if full advantage of their high sensitivity is to be realized.

A practical design procedure for selecting a thermistor for use in a kath-

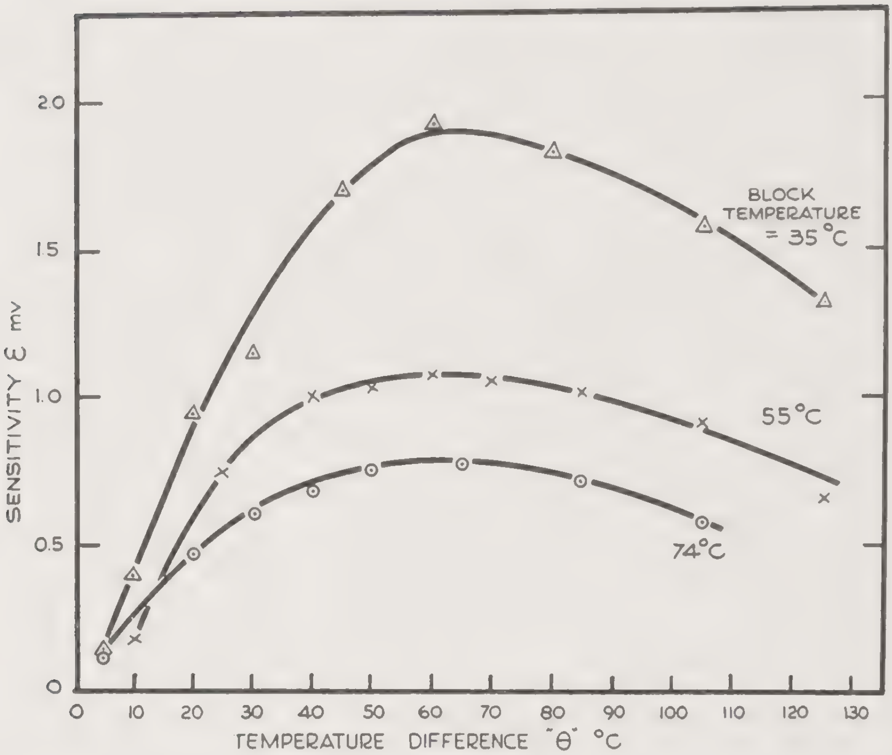


FIG. 20. Effect of block temperature on sensitivity (R_{25} = 2000 ohms).

arometer requires the following information additional to that on the thermistors themselves:

1. Expected fractional change in thermal conductivity $\Delta K/K$ or range thereof.
2. Possible full scale deflections of the indicating or recording instruments likely to be used together with the other specifications of the instruments, i.e., input impedance, speed of response, accuracy, etc.
3. Type of katharometer and its probable time-constant.
4. Proposed temperature regulation and operating temperature of the cell block.
5. Proposed bridge supply, power rating, output voltage, and regulation.

The plot shown in Fig. 13 or a similar plot may be rescaled in terms of millivolts per unit change in $\Delta K/K$ and then it can be used as an approximate design chart to estimate the probable output in millivolts to be expected for a given value of $\sqrt{R_{25}(P/\theta)}$. The $\Delta K/K$ change in Fig. 13 was 5.8×10^{-3} and the chart can be generalized by dividing the ordinates by this quantity. It must be stressed however that this chart would only apply exactly to katharometers of similar geometry operating at the same cell block temperature (35°C). A correction for a different cell block temperature can be estimated from Fig. 20. Baker *et al.* (*1*) have shown that the sensitivity of a similar thermistor katharometer when measuring gas chromatographic peaks depends upon the position of the thermistor bead and that slightly higher sensitivities and improved resolution can be achieved by placing the thermistor directly in the gas stream. However, this would tend to increase the "flow" noise and would require closer control of gas flow rate and carrier gas temperature so that a compromise must be sought for small signal levels. The slightly longer time-constant of the diffusion-fed cell enables a thermistor of larger dissipation constant to be used so that the loss in sensitivity can be recovered but the slight loss of resolution remains. This loss in resolution can be serious if the diffusion path is too long and this effect is more pronounced with the heavier carrier gases. The experiments reported in this paper were not position sensitive as the gas streams were switched and the final steady values determined so that diffusional mixing effects were absent.

The selection of the millivolt recorder range determines the output required and the probable range of $\sqrt{R_{25}(P/\theta)}$ can be estimated. Since (P/θ) is usually given in mw/°C, R_{25} is best expressed in terms of KΩ to give the correct product numerically.

The time-constant of the katharometer for the particular carrier gas to be employed enables a value for the upper limit of the thermistor time-constant, and thus the dissipation constant, to be estimated. The thermistor thermal time constant is the time required for the thermistor to change its temperature 63 % of an applied step change in temperature, similarly the katharometer time constant is the time required for the katharometer to indicate 63 % of the applied composition step change. Typical values for a temperature difference of 50°C and a cell block temperature of 35°C are 6–8 seconds for nitrogen and 1–2 seconds with hydrogen. The "time-constant" of the katharometer depends upon the operating temperature, temperature difference, and the nature of the secondary component and carrier gas. For optimum response the thermistor time-constant should be one half to one quarter that of the overall cell time-constant. The thermal time-constant and the dissipation constant are approximately related by geometric factors since the specific heat capacities of most thermistor materials are similar, so that an approximate correlation can be made. Flakes have higher dissipation constants than beads of the same mass and usually have smaller thermal time-constants so that shape must be considered. However, flakes are usually bare oxides and the greater chemical stability of glass coated beads may off-set their larger time-constants in some applications. If the application is critical the porosity of the glass coating should be examined. Thermistors slowly degrade when operated in hydrogen above 100°C but may be cautiously operated at lower temperatures (*circa* 90°C) depending upon the nature of the particular oxide material used. All such applications should be checked experimentally by exposure to flowing hydrogen over an extended period.

The input resistance of the millivolt recorder allows an upper limit of usable thermistor resistance to be estimated.

The thermistor resistance at 25°C should correspond to a value at the operating temperature (i.e., cell block temperature plus 50°C) which lies in a range from twice to one half of the input resistance of the recorder. (The condition for maximum power transfer and perfect matching is that the thermistor resistance at the operating temperature should equal the input resistance of the recorder). This defines a range of resistance values and the manufacturer's lists may be searched for thermistors with suitable values of R_{25}, $\sqrt{R_{25}(P/\theta)}$ and time constant. The specifications for matching pairs of thermistors can be calculated from the temperature and voltage regulation by means of the relationships given in Appendix A. This procedure is best outlined by a specific example. Consider the following typical application:

A diffusion type katharometer is to be used in conjunction with a gas chromatographic apparatus using helium as a carrier gas. The apparatus is to monitor C_1–C_4 hydrocarbon mixtures and the concentration at the detector will be about ½% hydrocarbon in helium. This would correspond approximately to a carrier gas flow rate of 20 cc per minute and a sample volume of 1 cc containing five components in approximately equal amounts. The column would be such that the duration time of a peak would be about two minutes.

(*i*) $\Delta K/K$ for such a mixture at the film temperature (60°C) would be $\simeq 4.2 \times 10^{-3}$.

(*ii*) Either a 10, 5, or a 2.5 mV F.S.D. recorder is available with zero offset of 5 × F.S.D. and input impedances of 400, 1,000, or 5,000 ohms and full scale traverse times of 1, 2, or 10 seconds.

(*iii*) The katharometer time-constant should not exceed five seconds.

(*iv*) The cell block temperature will be 35 ± 0.1°C.

(*v*) The bridge voltage supply will be 40 volts ± 0.2%.

From Fig. 13 the values of $\sqrt{R_{25}(P/\theta)}$ corresponding to 2.5, 5, and 10 mV output can be estimated.

(*i*) 2.5 mV would require approximately $0.6 \times \dfrac{4.2 \times 10^{-3}}{5.8 \times 10^{-3}} \simeq 0.43$

$$= \sqrt{R_{25}(P/\theta)_{He}}$$

(*ii*) 5 mV would require approximately $1.7 \times \dfrac{4.2 \times 10^{-3}}{5.8 \times 10^{-3}} \simeq 1.23$

$$= \sqrt{R_{25}(P/\theta)_{He}}$$

(*iii*) 10 mV would require approximately $3.8 \times \frac{4.2 \times 10^{-3}}{5.8 \times 10^{-3}} \simeq 2.75$

$$\times \sqrt{R_{25}(P/\theta)_{He}}$$

$$\text{i.e. } R_{25}(P/\theta)_{He} = (i)\ 0.21, \quad (ii)\ 1.51, \quad (iii)\ 7.6.$$

A five second time-constant would require a thermistor time-constant of approximately 2.5 to 1.25 seconds and this would correspond to a dissipation constant of about 0.5 mW/°C in air for one particular size of bead thermistor. The dissipation constant in carrier gases other than air is given approximately by

$$(P/\theta)_{\text{gas}} = (P/\theta)_{\text{air}} \cdot \frac{\text{Thermal conductivity of gas}}{\text{Thermal conductivity of air}}.$$

Thus $(P/\theta)_{He} \simeq 5.5\ (P/\theta)_{\text{air}}$ so that possible ranges of R_{25} would be (*i*) 40 to 160 ohms, (*ii*) 300 to 1200 ohms, (*iii*) 1,500 to 6,000 ohms.

The thermistor operating temperature would be 85°C (cell block temperature +50°C for optimum θ) and at this temperature the resistance $R \simeq 0.14\ R_{25}$ (for a common thermistor material).

This means that recorders with input resistances of (*i*) 6 to 22, (*ii*) 40 to 170, (*iii*) 210 to 840 ohms would be required and from the thermistor time-constant of 1.25 to 2.5 seconds the two seconds full scale traverse instrument might be chosen. A suitable thermistor for use with the 10 mV instrument would be 2,200 ohms with a dissipation constant of 0.7 mW/°C and a time-constant of 2 seconds. This would be used in conjunction with a 10 mV recorder of one second for full scale traverse and an input resistance of 400 ohms. The relationship between time-constant and dissipation constant differs from type to type but approximate relationships can be obtained for a given bead size and lead configuration by examination of manufacturer's data lists.

The thermistors should be matched so that the error due to temperature and voltage fluctuations is not to exceed 0.5% of F.S.D., i.e., an error of 50 μV from both sources or 25 μV from each individual source.

The bridge voltage E for a four equal arm bridge is calculated from the dissipation constant 0.7 mW/°C in air corrected by the relative thermal conductivity of helium to air (5.54) at the film temperature (60°C) and the known resistance at the operating temperature 308 ohms and the temperature difference θ of 50°C.

$$E \simeq 15 \text{ volts.}$$

The percentage change of resistance with temperature is approximately

4% for this thermistor material so that the tolerance β may be obtained from Eq. 11 in Appendix A.

$$\bar{\epsilon} = \frac{E}{8}\cdot\frac{0.5\Delta T}{10^4}\cdot(\%\ R/^\circ\mathrm{C})\beta$$

(a) $$25 \times 10^{-6} = \frac{15}{8} \times \frac{0.5 \times 0.1}{10^4} \times 4 \times \beta$$

$$\beta \simeq \underline{0.7\%}$$

This would be too stringent a requirement and it would be necessary to improve the thermostatting to ±.04°C if possible, which would relax the tolerance on β to $\pm 2\%$.

For voltage changes the matching conditions are given in Eq. 7 of Appendix A.

$$\bar{\epsilon} = \frac{E^2}{1600}\cdot\Delta E\cdot\left[\frac{(\%R/^\circ\mathrm{C}}{R\cdot(P/\theta)}\right]\cdot\frac{\alpha}{100}$$

ΔE is 0.2% of the bridge voltage E.

$$25 \times 10^{-6} = \frac{15^3}{1600} \times \frac{2 \times 10^{-3}}{100} \times \left[\frac{4}{0.308 \times 5.54 \times 0.7}\right] \times \alpha$$

$$\alpha \simeq 0.18\%$$

This again would be too stringent a requirement and the voltage regulation should be improved to ±0.005% which would allows a tolerance of ±8% for α_{He} or ±1.5% for α_{air}.

The resistances should be matched so that the bridge is sufficiently close to balance for the 5 × F.S.D. zero offset adjustment to compensate. Allowance should be made for slight aging drifts so that only half of the available offset should be considered available for initial zero adjustment. Assuming a four-arm equal bridge with matched detector the out-of-balance voltage is given by Eq. 5 of Appendix A.

$\bar{\epsilon} = (E/8)\cdot(\Delta R/R)$, and this may be written as

$\epsilon = (E/800)\cdot\gamma$ where γ is the percentage mismatch in resistance.

$$25 \times 10^{-3} = 15/800\cdot\gamma$$

$$\gamma = 1.5\%$$

The Wheatstone bridge is usually adjusted to zero indication by adjusting the resistive bridge arms to balance and not by off-setting the zero of the millivolt recorder. However, it should be realized that in the asymmetric bridge exact compensation for reference composition changes and temperature and voltage changes will not in general be attained. The nonlinearity of the out-of-balance signal may be calculated from the equations given in Appendix B.

If the improved temperature and voltage regulations were realized the final tolerances for the thermistors would read as follows.

Matched pairs to be supplied with:

(1) 2,200 ohm resistance matched within 1%,

(2) percentage change of resistance per degree Centigrade to be matched within ± 2%,

(3)
$$\left[\frac{(\%R/°\mathrm{C})}{R_{25}(P/\theta)_{\mathrm{air}}}\right]$$

to be matched within ±2% or thermal time constants or dissipation constants to be matched within ±1%. The quantity

$$[(\%R/°\mathrm{C})/R_{25}(P/\theta)]$$

is best examined by changing the bridge voltage slightly when the thermistors are at operating temperature in the gas in which they are to be used and observing the change in out-of-balance voltage.

To close, we hope that in presenting this paper we have fulfilled our aim, which was to discuss some of the factors which influence the choice of a thermistor for a particular application and to indicate how to choose the best operating conditions for an existing katharometer.

Acknowledgment

This work was carried out at the Central Research Laboratory of Canadian Industries Limited and we wish to thank Dr. I. R. McHaffie, Research Department Manager for permission to publish and our colleagues for much helpful discussion, especially Dr. S. S. Grimley who supervised the work. Acknowledgement is due to Dr. D. McEwen who kindly furnished the material for Figs. 1 and 2 and to Mr. L. Forgues who assisted with the experimental work.

APPENDIX A

CALCULATION OF MATCHING TOLERANCES FROM THE VOLTAGE AND TEMPERATURE REGULATION

Consider a four equal arm bridge with a matched detector (millivolt recorder) of input resistance R_5 such that $R_1 = R_2 = R_3 = R_4 = R_5$. (See Fig. 21A.) Let the voltage change by a quantity ΔE so that the power to thermistors R_3, R_4 changes.

$$\text{Power change} = \frac{(E + \Delta E)^2}{4R_{3,4}} - \frac{E^2}{4R_{3,4}} \simeq \frac{E \cdot \Delta E}{2R_{3,4}} \qquad (1)$$

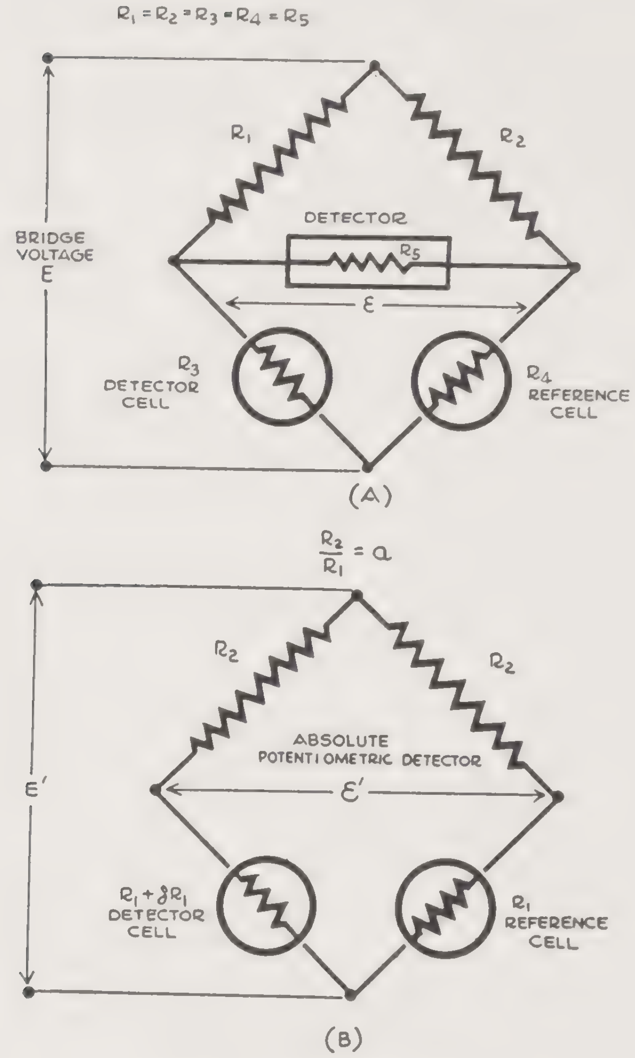


FIG. 21. Bridge arrangement.

This causes a temperature change $T_{3,4}$

$$\Delta T_{3,4} = \frac{E \cdot \Delta E}{2R_{3,4}(P/\theta)_{3,4}} \tag{2}$$

where $(P/\theta)_{3,4}$ is the dissipation constant in watts/°C not in mW/°C. This temperature change causes a change of resistance

$$\Delta R_{3,4} = \left(\frac{\partial R}{\partial T}\right)_{3,4} \cdot \Delta T_{3,4} \tag{3}$$

and the fractional change of resistance is

$$\left(\frac{\Delta R}{R}\right)_{3,4} = \left\{\frac{1}{R_{3,4}}\left(\frac{\partial R}{\partial T}\right)_{3,4}\right\} \Delta T_{3,4} \tag{4}$$

The quantity $[(100/R_{3,4})\cdot(\partial R/\partial T_{3,4})]$ is the percentage change in resistance per degree Centigrade ($\%\ R/°\mathrm{C}$) which is usually given by the manufacturer.

The out-of-balance voltage for a bridge with a one active arm and matched detector is (*2*):

$$\epsilon = \frac{E}{8}\cdot\frac{\Delta R}{R} \tag{5}$$

and if $(\Delta R/R)_3 = (\Delta R/R)_4$ then the thermistors are matched and the resultant out-of-balance voltage $\bar{\epsilon} = \epsilon_3 - \epsilon_4$ due to the change ΔE in E the bridge supply voltage will be zero and from Eqs. (2), (4), and (5)

$$\bar{\epsilon} = \frac{E}{8}\cdot\frac{E\cdot\Delta E}{200}\left\{\frac{1}{R_3\cdot(P/\theta)_3}\left[\frac{100}{R_3}\left(\frac{\partial R_3}{\partial T}\right)\right] - \frac{1}{R_4\cdot(P/\theta)_4}\left[\frac{100}{R_4}\left(\frac{\partial R_4}{\partial T}\right)\right]\right\} \tag{6}$$

This may be rewritten as

$$\bar{\epsilon} = \frac{E^2}{1600}\cdot\Delta E\cdot\left[\frac{(\%R/°\mathrm{C})}{R\cdot(P/\theta)_3}\right]\cdot\frac{\alpha}{100} \tag{7}$$

where α is the percentage mismatch of $(\%\ R/°\mathrm{C})/R\cdot(P/\theta)$ between the two thermistors.

The tolerances on matching the coefficient of resistance change with temperature can be calculated from the temperature regulation if the desired error in out-of-balance voltage is stated. If one assumes that a variation ΔT in the cell block temperature is directly transmitted to the carrier gas and directly affects the thermistor then a one to one correspondence in thermistor temperature fluctuation and cell block temperature fluctuation would result. This is equivalent to assuming that heat is lost from the thermistor in only one way and that the cell block is the sole heat sink. In reality part of the heat is removed by the flowing gas and it is necessary to specify the exact geometry and mechanism of heat transfer if the functional relationship between the cell block temperature fluctuations and the thermistor temperature fluctuations is to be solved; an exact solution may be impossible. An approximate relationship

$$\Delta T_{\mathrm{Thermistor}} = A\cdot\Delta T_{\mathrm{Cell\ block}} \tag{8}$$

may be written and A will lie between 0 and 1. For a diffusion type cell A will be taken to be about 0.5. A change in cell block temperature ΔT will cause a fractional change of resistance

$$\left(\frac{\Delta R}{R}\right)_{3,4} = A\cdot\left\{\frac{1}{R_{3,4}}\left(\frac{\partial R}{\partial T}\right)_{3,4}\right\}\Delta T \tag{9}$$

and the resultant out-of-balance voltage, $\bar{\epsilon} = \epsilon_3 - \epsilon_4$, will be

$$\bar{\epsilon} = \frac{E}{8} \cdot \frac{A \cdot \Delta T}{100} \left\{ \left[\frac{100}{R_3} \left(\frac{\partial R_3}{\partial T} \right) \right] - \left[\frac{100}{R_4} - \left(\frac{\partial R_4}{\partial T} \right) \right] \right\} \tag{10}$$

which may be written as

$$\bar{\epsilon} = \frac{E}{8} \cdot \frac{0.5 \Delta T}{100} \cdot (\% R/{}^\circ C) \cdot \frac{\beta}{100} \tag{11}$$

where β is the percentage mismatch in the temperature coefficient of resistance ($\%\ R/{}^\circ\mathrm{C}$).

Equation (11) allows the error in out-of-balance voltage to be determined for given mismatch β in the temperature coefficients of resistance of the thermistors.

APPENDIX B

Conditions for Optimum Bridge Sensitivity

The conditions for maximum sensitivity and precision for galvanometric detectors are that the four arms should be of equal resistance and the galvanometer resistance should be equal to the bridge arm resistance. This is also the condition for maximum power transfer between the bridge and detector.

With this type of detector a bridge with four parameter varied arms is often used to obtain twice the sensitivity possible with two parameter varied arms of similar construction.

If a potentiometric detector is used then the conditions for maximum sensitivity are somewhat different (*3*). For a given detector and compensating cell resistances the out-of-balance voltage ϵ may be increased slightly by employing an increased voltage E' (compared with the equal arm bridge value E) and using the parallel arrangement shown in Fig. 21B.

The out-of-balance voltage ϵ' for this arrangement is given by

$$\begin{aligned}
\epsilon' &= \left\{ \frac{R_1 + \delta R_1}{R_1 + \delta R_1 + R_2} - \frac{R_1}{(R_1 + R_2)} \right\} E' \\
&= \left\{ \frac{R_1 + \delta R_1}{(R_1 + R_2)(1 + \delta R_1/(R_1 + R_2))} - \frac{R_1}{(R_1 + R_2)} \right\} E' \\
&= \frac{E'}{(R_1 + R_2)} \left\{ (R_1 + \delta R_1) \left(1 - \frac{\delta R_1}{(R_1 + R_2)} + \frac{\delta R_1^{\,2}}{(R_1 + R_2)^2} + r - R_1 \right\} \right. \\
&= \frac{E' \delta R_1}{(R_1 + R_2)} \left\{ 1 - \frac{R_1}{(R_1 + R_2)} - \frac{\delta R_1}{(R_1 + R_2)} \left(1 - \frac{R_1}{(R_1 + R_2)} \right) \right\}
\end{aligned}$$

and if $R_2 = aR_1$

$$\epsilon' \simeq \frac{E'}{a + 1} \cdot \frac{\delta R_1}{R_1} \left\{ \frac{a}{a + 1} - \frac{\delta R_1}{R_1} \cdot \frac{a}{(a + 1)^2} \right\}, \text{ neglecting } \delta R_1^{\,2}, \text{ etc.}$$

The lack of linearity for a given change δR_1 or the maximum possible δR_1 for a given error x can be obtained from the second term in the equation for ϵ'.

$$\delta R_1 = (a + 1)\ R_1 x, \qquad (\delta R_1 = 2R_1 x \text{ for equal arms})$$

If "a" > 1 and if the bridge voltage is adjusted so that the same current flows in R_1 so that the thermal conditions are unchanged then

$$E' = \frac{(a+1)}{2} E$$

$$\epsilon' = \frac{2a}{(a+1)} \epsilon.$$

Therefore by using a higher voltage supply E' and maintaining the current through the bridge at a value which maintains equivalent thermal conditions, slightly higher sensitivities can be attained and the linearity can be improved if a truly potentiometric detector is used. The following table gives typical values:

a	1	3	5	7	9	19	49
Bridge voltage increased by factor	1	2	3	4	5	10	25
% Increase in sensitivity	0	50%	66.7%	75%	80%	90%	96%
Relative nonlinearity	1	0.5	0.33	0.25	0.20	0.10	0.04

The choice of a is determined by the availability of suitable power supplies. If the bridge is normally powered from storage batteries it becomes inconvenient to increase the bridge voltage by large factors but this does not apply to electronically stabilized power supplies which operate best at higher voltages. This form of bridge arrangement, using a parallel feed through large resistors, is to be preferred when using thermistors since the likelihood of thermal runaway is diminished. Furthermore the changes in bridge current are much smaller for the parallel arrangement than for the series bridge (i.e., detector and power supply interchanged) so that regulation is better when electronic power supplies are used. The series arrangement, which places the detector across the junction of the two low resistances and the two high resistances, and which gives maximum sensitivity if a galvanometric detector is used (Callendar's criterion), is thermally unstable if thermistors are used. In the parallel arrangement the resistances may be chosen so that the maximum current through the bridge arms does not exceed the maximum rating of the thermistors used.

Dimbat *et al.* (*3*) have shown that the use of four parameter varied arms of a given resistance R_a and a potentiometric detector does not give the maximum signal output possible from four thermal elements and the dual parameter-varied arm parallel feed bridge with two cells in series (arm resistance = 2 R_a) can be made to give a larger output and to possess better linearity if the bridge supply voltage is increased whilst maintaining identical thermal conditions in the katharometer.

The usual self-balancing recorder is only truly potentiometric (i.e., draws zero current) at balance. When moving to a balance-point or when following a rapidly changing potential it will possess an effective impedance close to the input resistance of the servo-amplifier, so that unless this is large compared to the bridge resistance the behavior will be intermediate between a galvanometric and a true potentiometric detector. Thus, the theoretical increase may not always be realizable with a self balancing potentiometric recorder. Amplifiers are available with high input impedances which remain constant whilst the potential changes and which will feed directly to a millivolt recorder of low input impedance and allow this increase in sensitivity and linearity to be realized.

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CHAPTER XIX

A Combustion Device for Use in Conjunction with Chromatographic Columns

STANLEY D. NOREM

The Perkin-Elmer Corp., Norwalk, Connecticut

The use of a copper oxide combustor to convert chromatographic hydrocarbon bands to carbon dioxide and water was probably first suggested by Martin and Smart (*1*). They used such a device in connection with an infrared detector sensitive to carbon dioxide. Such a device is not limited to this application, however, and would appear to be useful in two ways:

1. As a "gas amplifier" for trace and/or high boiling hydrocarbons. The combustor, placed at the outlet of a chromatographic column, converts the eluent peaks to carbon dioxide and water, with a corresponding increase in number of molecules reaching the detector. Thus, each molecule of, for example, toluene, would be converted to seven molecules of carbon dioxide and four molecules of water.

2. As a device for elemental analysis of hydrocarbon samples. The combustor is placed ahead of a column which is capable of separating carbon dioxide and water. This sort of arrangement, properly calibrated, would yield qualitative information such as the carbon-hydrogen ratio of a fuel sample, or the identity of pure samples.

The apparatus used consisted of a piece of ¼-inch stainless steel tubing about 15 cm in length, wrapped with fiberglass cloth, nichrome heater wire, and another layer of glass cloth. A chromel-alumel thermocouple was silver soldered to the outside of the tube. As the tube was separated from the heater wire by a layer of glass cloth, this was felt to be capable of giving a reasonably good indication of the temperature of the contents of the tube. The ends of the tube were fitted to accept ⅛″ stainless tubing. The ⅛″ tubing, bent into loops, served to isolate the combustor thermally from the detector. The entire device was about the size of a one meter column and could, therefore, be used in a standard Model 154 Vapor Fractometer, either before or after a standard column. The combustor tube was filled with various grades of copper oxide and copper oxide-firebrick mixes. Temperature was adjusted by means of a powerstat.

Three basic tube fillings were tried:

1. A short (about 2 or 3 cm) length of tube was filled with fine, powdered copper oxide. This was an effective combustor, but had the disadvantage

of restricting the flow considerably, particularly at combustion temperatures.

2. The entire length of the tube was filled with copper oxide wire (Baker Chemical Co.). About 6 g was required to fill a 15 cm tube. This had desirably low flow impedance, but insufficient active area to completely convert stable compounds such as methane at normal flow rates.

3. A mixture of firebrick and fine copper oxide was used as a compromise. About 50% by weight copper oxide (1 g) appeared to be the upper limit consistent with a reasonably uniform mixture. This mix converted methane satisfactorily at normal flow rates.

The obvious filling would be the proper particle size of pure copper oxide. This does not seem to be as readily available as one would expect.

Another possibility might be a blend of fine copper oxide and Celite, which may be a better support than firebrick.

The operating temperature of the combustor was determined by observing the degree of conversion of methane with gradual temperature increases. Virtually no conversion occurs very much below 600°C. At about 700°C, the conversion is complete. An operating temperature of 750°C (nominal) was used to avoid the consequences of temperature measurement errors. This agrees with references in the literature. Regeneration of the combustor was accomplished by passing an air carrier through the instrument with the copper oxide at 750°C.

It was apparent from the outset that the theoretical "gain" was not being realized. For example, methane (theoretical gain of 3) gave a gain of 2.23; pentane, (theoretical gain of 11) a gain of only 2.24. This shortcoming was at first attributed to the combustor. The combustor was then placed ahead of a molecular sieve column and methane was introduced. Since a molecular sieve column will retain water and carbon dioxide indefinitely, but will pass methane, the almost complete disappearance of even 5 cc of methane was accepted as proof that the conversion was complete.

The combustor was then placed ahead of a 2 meter "A" column which will separate carbon dioxide and water. A sample of toluene was introduced and converted. Since toluene has a longer retention time than water, complete conversion was verified by the absence of any trace of toluene. Samples of carbon dioxide and water in the same amount as the expected yield from the converted toluene were introduced and checked within the limits of sample reproducibility. The failure to achieve the expected gain was seen to be due to three facts:

1. The thermal conductivity of carbon dioxide is higher than that of most samples, and the thermal conductivity of water vapor is much higher than that of most samples.

2. The response of the detector is not linear over the wide range involved in converting a large sample of a heavier hydrocarbon.

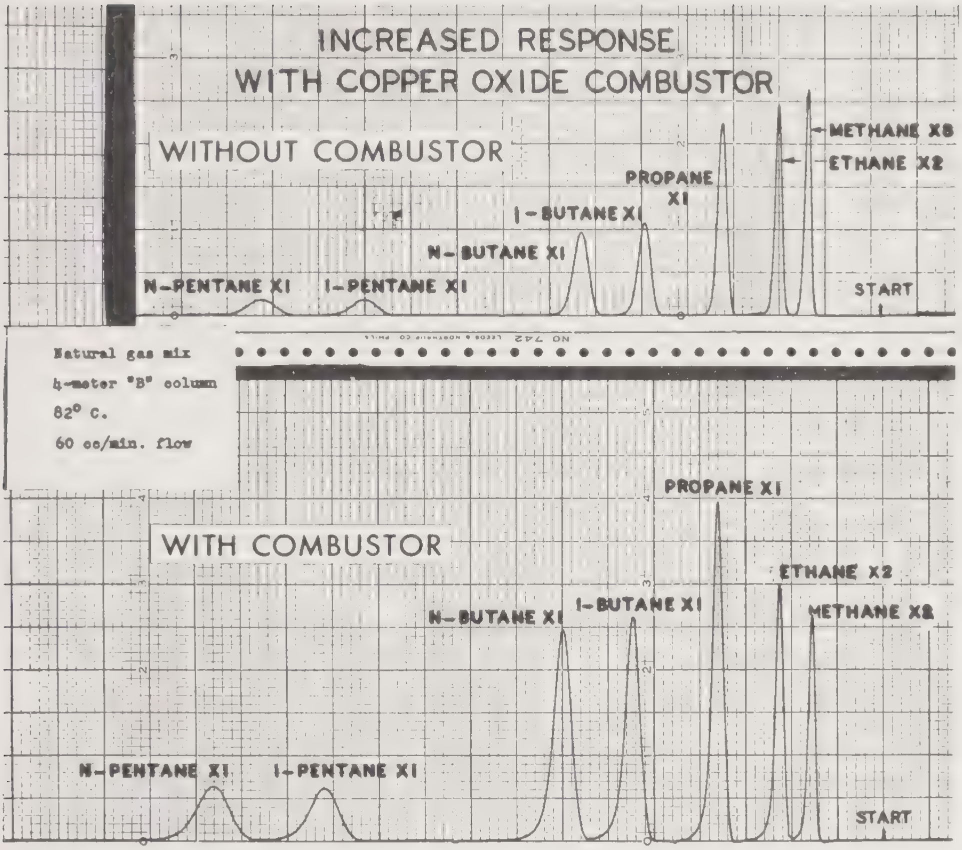

FIG. 1. Comparative runs showing the peak height amplification obtained by placing a copper oxide combustor between the outlet of a chromatographic column and the inlet of a thermal conductivity detector.

3. The water vapor resulting from the combustion does not emerge as a clean peak but tails noticeably as a result of adsorption upon metal surfaces.

A series of runs was then made using 1/4 cc gas samples. The first run, with the combustor unheated, was to measure the relative response of the detector to various samples. The results are summarized in the following table.

Sample	Peak Height	Normalized Peak Height
Methane	28	0.76
Ethylene	38	1.13
Propane	57.5	1.56
Isobutane	68	1.84
Carbon dioxide	37	1.00

The same samples were then run with the combustor at 750°C and the peak heights of the resultant carbon dioxide bands measured. The results are shown below.

Sample	Peak Height of Resultant Carbon Dioxide	Normalization
Methane	33	1.02
Ethylene	65	2.00
Propane	97	3.00
Isobutane	132	4.06
Carbon dioxide	32.4	1.00

The extreme asymmetry of the water peaks discouraged any accurate measurements of them.

The column and combustor were interchanged and the carbon dioxide plus water peak height measured. The water caused pronounced band tailing as previously noted. Another point of interest is that the gain was in some cases actually less than that of the carbon dioxide band alone.

Sample	Carbon Dioxide Gain	"Total" Gain
Methane	1.32	1.17
Ethylene	1.76	1.61
Propane	1.92	1.92
Isobutane	2.20	2.12

CONCLUSIONS

1. This device, as a gas amplifier, will not provide as high gains as one might expect. According to Rosie and Grob (*2*), the response of a thermal conductivity detector increases linearly with the square root of the molecular weight of the sample. This means that the gain of our "gas amplifier" will vary in roughly the same way. The contribution of the water vapor is not clear due to the poor band shape obtained in these experiments, but it does not appear to be great and may actually detract from the gain obtainable from the carbon dioxide alone.

2. Used in conjunction with a suitable column, the combustor as a means of elemental analysis seems to have considerable potential.

3. Another use of the combustor might be to avoid detector contamination when heated columns (at higher-than-detector temperatures) are used.

The two runs shown in Fig. 1 demonstrate the sort of "gas amplification" that may be realized with this device.

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CHAPTER XX

The Effect of the Ratio of Partition Liquid to Inert Support on the Separation of (1) Mono-, Di-, and Triethylene Glycols and (2) *Cis-* and *Trans-*2,5-Dimethylpiperazine

RUSSELL D. RING

Wyandotte Chemicals Corporation, Wyandotte, Michigan

INTRODUCTION

The variables affecting the separation of volatile liquids or gases by gas chromatography are recognized as column temperature, column length, chemical character of the partition liquid, and carrier gas flow rate. Proper application of these variables usually results in the separation of the desired components of a mixture in the shortest possible time. The chemical character of the partition liquid is perhaps the most useful variable available to the chromatographer and, indeed, it is this variable that makes gas chromatography such a useful analytical tool.

Although the weight per cent of partition liquid on inert support is discussed by several authors, most investigations have been conducted using a fixed amount of from 15 to 40 weight per cent (*1–4*). In most cases the selected ratio of partition liquid to inert support, together with the proper selection of the other variables, yield the desired results. Keulemans and Kwantes (*5*) investigated the effect of the amount of partition liquid on the separation of propane, isobutane and *n*-butane and found that the highest column efficiency was obtained using 15–20 weight per cent hexadecane as the partition liquid.

As the operating temperature of a gas chromatograph is raised to higher temperatures, the selection of the proper partition liquid is hindered by such things as lack of thermal stability and too high a vapor pressure. The end result is that the thermal stability and vapor pressure sometimes govern the selection of the partition liquid, not its chemical character.

It is the purpose of this paper to discuss the effect of the ratio of partition liquid to inert support on the separation of mono, di-, and triethylene glycols and on the separation of *cis-* and *trans-*2,5-dimethylpiperazines. The latter example is included to show the effect of this variable on the peak symmetry or distribution isotherm of *cis-*2,5-dimethylpiperazine. An additional application of this effect is presented in the separation of ethylene glycol and diethylene glycol monoethyl ether.

EXPERIMENTAL

A model K-2 Kromo-Tog made by the Burrell Corporation of Pittsburgh, Pennsylvania, was used for this investigation.

The columns used were standard U-shaped, glass, and heated electrically. The first two inches of the column were insulated with asbestos to provide a simple flash heater. The column packing was prepared by the solvent-slurry method employing methanol as the solvent (*2*). The inert support used was Johns-Manville C-22 fire brick, ground and sieved to remove all but the 30 to 60 mesh particles.

The partition liquids used were Carbowax 1000 (a polyethylene glycol), Flexol 8N8, [2,2′(2-ethylhexamido)diethyldi(2-ethylhexoate)], both made by Union Carbide and Carbon and tetrahydroxyethylethylenediamine made by the Visco Products Co., Inc. of Houston, Texas.

Sample injection was made by means of a standard "Alga" micrometer syringe. The plug joining the syringe barrel to the hypodermic needle was made from Teflon in order to accommodate standard size hypodermic needles.

RESULTS

The chromatograms shown in Fig. 1 illustrate the effect achieved in the separation of a mixture of glycols by reducing the amount of partition liquid from a ratio of 0.45:1.00 to 0.12:1.00. At a ratio of 0.45:1.00, complete separation of the glycol mixture was obtained but the triethylene glycol peak was broad and difficult to integrate. When the ratio was reduced to 0.12:1.00, and still operating at the same column temperature of 180°C, the peaks were blended together due to their more rapid elution from the column. Retaining the same ratio of 0.12:1.00, the column temperature was reduced to 150°C. With the amount of partition liquid reduced by one-third, it was possible to reduce the time of the run, obtain sharper peaks and still retain complete resolution even though operating at a lower column temperature of 150°C.

The chromatograms shown in Fig. 2 illustrate the effect of a lower column temperature on the separation of *cis*- and *trans*-2,5-dimethylpiperazines. At a column temperature of 125°C only partial separation was obtained and the *cis*-2,5-dimethylpiperazine peak tailed noticeably. When the column temperature was reduced to 100°C a better separation was obtained, but both peaks tailed so much so as to render valueless an analytical procedure based on these conditions.

Figure 3 illustrates the effect obtained with the same system when the amount of partition liquid was reduced from a ratio of 0.45:100 to 0.12:1.00. The most noticeable effect was the improved symmetry of the *cis*-2,5-dimethylpiperazine peak. The 100-cm column used did not give the desired degree of separation so it was necessary to change to a 250-cm column. Adjustment of the operating parameters now gave a satisfactory separation of the two isomers and could be used to set up an analytical method.

Tetrahydroxyethylethylenediamine (THEED) was found to have ex-

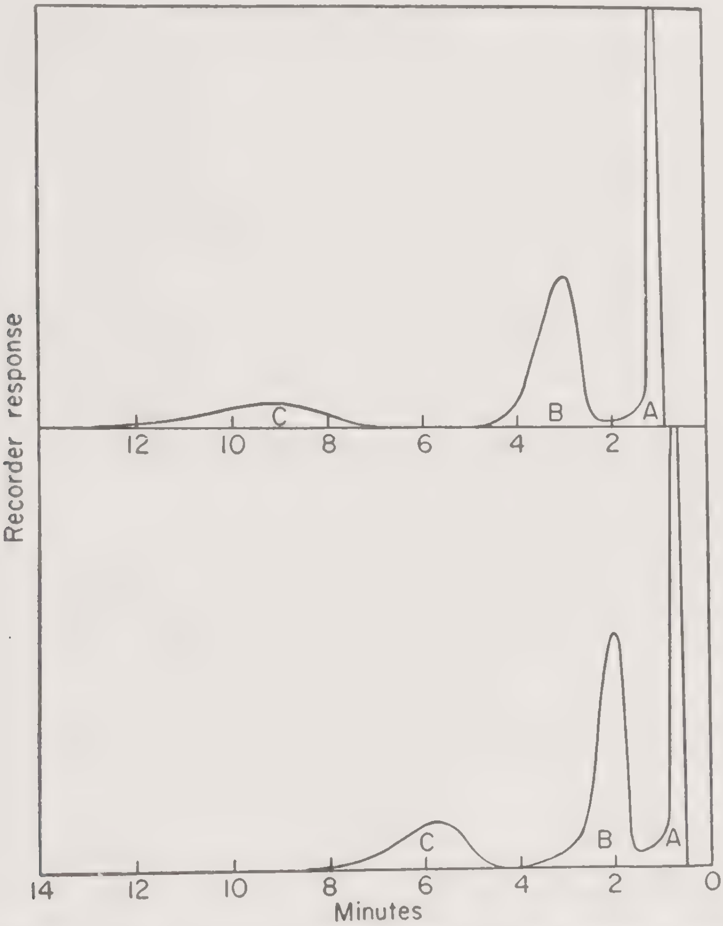

FIG. 1. Effect of the ratio of partition liquid to inert support. Mono-, di-, and triethylene glycols.

Ratio 0.45:1.00

Liquid	Carbowax 1000
Column length	60 cm
Column temperature	180°C.
Flow rate	95 ml He/min
Sample size	0.01 ml

Ratio 0.12:1.00

Column temperature	150°C.

A. Ethylene glycol, b.p. 197°C.
B. Diethylene glycol, b.p. 245°C.
C. Triethylene glycol, b.p. 287°C.

ceptionally strong hydrogen bonding properties and was used to separate ethylene glycol and diethylene glycolmonoethyl ether found in a commercial glycol ether. A ratio of 0.45:1.00 gave complete separation, but the ethylene glycol was retarded to such a degree that its peak was too broad

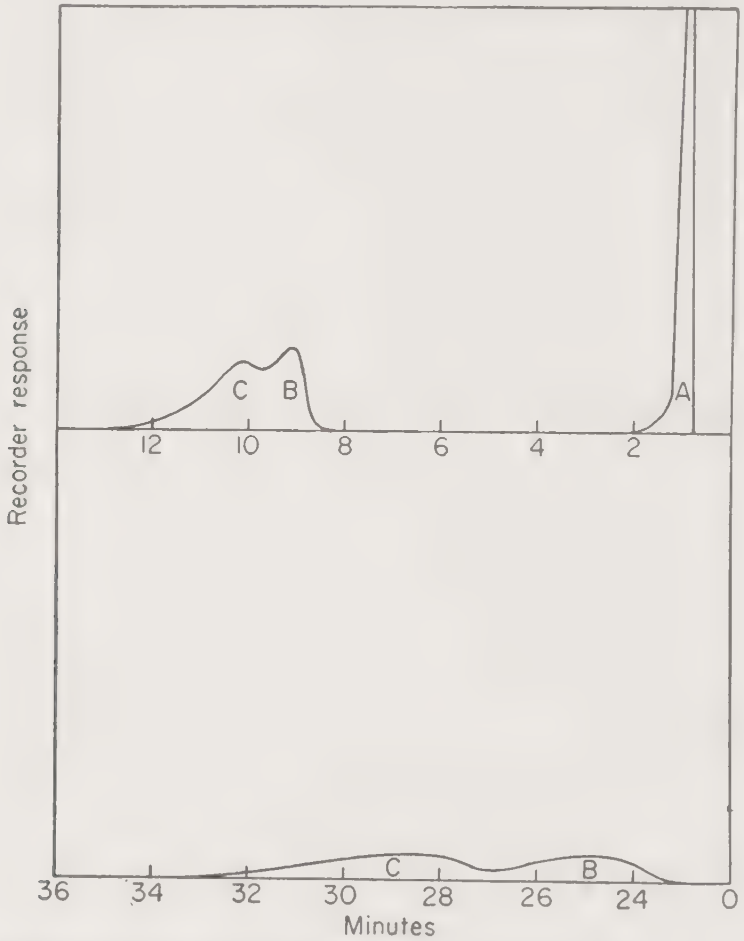

FIG. 2. Effect of column temperature on the separation of *cis*- and *trans*-dimethylpiperazines.

Liquid	Flexol SNS
Column Length	100 cm
Column temperature	125°C.
Flow rate	60 ml He/min
Sample size	0.005 ML (1:1 Dimethylpiperazines:ethanol)
Column temperature	100°C.
Flow rate	70 ml He/min

A. Ethanol
B. *Trans*-2,5-Dimethylpiperazine
C. *Cis*-2,5-Dimethylpiperazine

for analytical use. Increasing the column temperature helped, but decomposition of the THEED then occurred. The ratio of partition liquid to support was then reduced to 0.12:1.00 and the desired separation was obtained using the same length column and column temperature. Figure 4 shows the results of this separation. The impurities, ethanol, and ethylene glycol monoethyl ether, were also separated.

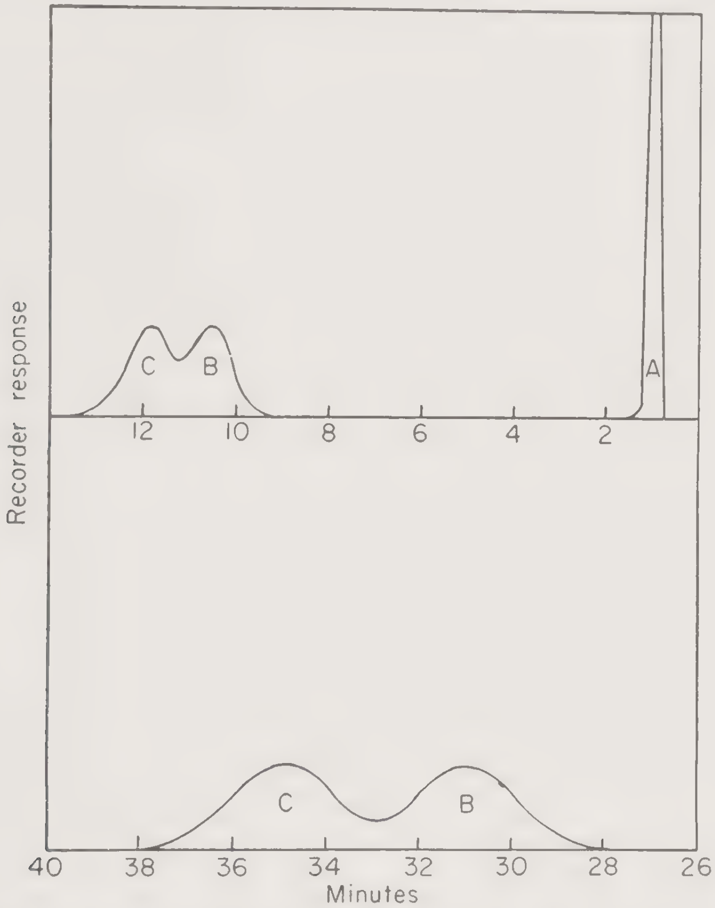

FIG. 3. Effect of temperature and column length on the separation of *cis*- and *trans*-2,5-dimethylpiperazines.

		Liquid	Flexol 8N8
		Column length	100 cm
Column length	250 cm	Column temperature	100°C.
Column temperature	100°C.	Flow rate	56 ml He/min
Flow rate	72 ml He/min	Sample size	0.005 ml

A. Ethanol
B. Trans-2,5-Dimethylpiperazine, b.p. 162°C.
C. Cis-2,5- Dimethylpiperazine, b.p. 165°C.

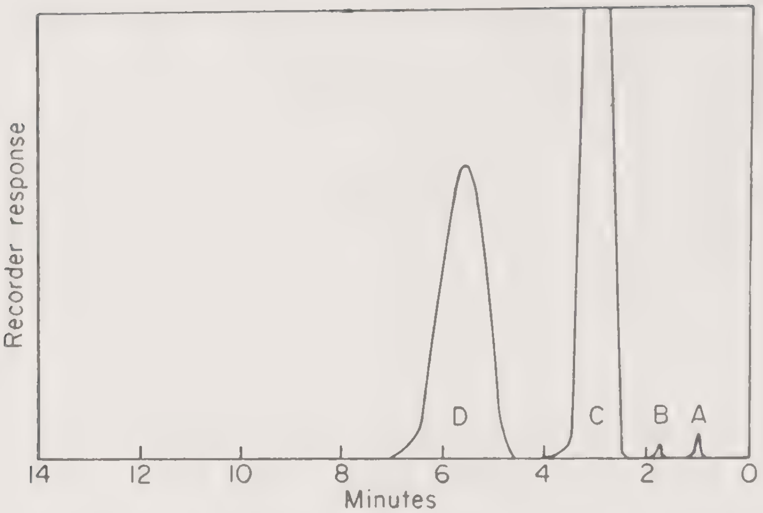

FIG. 4. Separation of commercial diethylene glycol monoethyl ether.

Liquid	THEED
Column length	100 cm
Column temperature	135°C.
Flow rate	78 ml He/min
Sample size	0.01 ml

A. Ethanol
B. Ethylene glycol monoethyl ether
C. Diethylene glycol monoethyl ether b.p. 195°C.
D. Ethylene glycol b.p. 197°C.

DISCUSSION OF RESULTS

In the examples presented, the effect of a change in the ratio of partition liquid to inert support is not the same. In the case of the glycols, the effect is one of reducing the time of analysis and producing sharper peaks and it can be said that the same effect would probably be obtained by using a shorter column. Each situation will probably require a different ratio of partition liquid to support to give optimum column efficiency. When peak symmetry and resolution are not affected a shorter column may be prepared by simply reducing the ratio of partition liquid to inert support.

Since most analytical methods are based on area measurement, the placement of the base line can lead to error in the case of very broad peaks. The sharper peaks obtained by a reduction of partition liquid reduce this possibility. Operation at a lower column temperature is desireable in cases where the thermal stability of the sample is critical.

The chromatographic separation of *cis-* and *trans*-dimethylpiperazines illustrates the effect of a reduction of the ratio of partition liquid to inert support on peak symmetry. Variation of the other operating parameters would not have produced the same effect. By reducing the amount of partition liquid by one-third, the distribution of the *cis* isomer between the partition liquid and the vapor becomes constant and a linear isotherm results. One possible reason for the nonlinear isotherm of the *cis* isomer is that its solubility in the partition liquid, at a ratio of 0.45:1.00, is not proportional to its vapor concentration. Under these conditions one would expect the resulting peak to have a sharp front and diffuse tail.

SUMMARY

The ratio of partition liquid to inert support has been shown to have a pronounced effect on the separation of mono-, di-, and triethylene glycols, and on the separation of *cis*- and *trans*-2,5-dimethylpiperazines.

A reduced time of analysis, sharper peaks and no loss in resolution were obtained for the mono-, di-, and triethylene glycols when the amount of partition liquid was reduced by one-third to a ratio of 0.12:1.00. The length of the column was the same but the column temperature could be reduced from 180° to 150°C.

In the case of the *cis*- and *trans*-2,5-dimethylpiperazines, the improved results could not have been obtained any other way except by reducing the amount of partition liquid. The improved symmetry of the *cis*-2,5-dimethylpiperazine, at a ratio of 0.12:1.00, can be attributed to a change in its liquid vapor distribution from a nonlinear to a linear function of the concentration.

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CHAPTER XXI

An Apparatus for Laboratory Preparative-Scale Vapor Phase Chromatography

J. J. KIRKLAND

Grasselli Chemicals Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware

Since the introduction of vapor phase chromatography (VPC) by James and Martin (*8*) in 1952, this versatile tool has found widespread usage for the semi-micro analysis of many types of complex mixtures containing components which boil as high as 400°C (*3*). Recently, several studies have been published (*1*, *2*, *5–7*, *11*) which describe the separation and purification of volatile compounds in quantities up to several grams. These papers have stressed the suitability of the method for the separation of pure substances, but the design of appropriate equipment was not given a detailed treatment. While this investigation was in progress, Whitham (*12*) reported on an analytical gas-liquid partition chromatographic apparatus using a column of 830 centimeters length and 12.7 millimeters internal diameter with which sample charges up to 3 cc were employed. Some construction details of this unit were given and several applications in the analysis of complex petroleum fractions and for the preparation of pure hydrocarbons were described.

The purpose of the present paper is to describe in detail a laboratory preparative-scale VPC apparatus which is capable of separating high-purity gases, liquids, and low melting solids in amounts up to 10 grams or larger. The readily constructed equipment employs columns of 31 mm I.D. in 6 ft-long sections to carry out the separation, and a thermal conductivity detector as a monitoring device. Isolation of fractions is accomplished with ease by means of a unique, highly efficient trapping system. Several applications of the described equipment to typical isolation and purification problems are discussed.

APPARATUS

A schematic diagram of the apparatus designed for preparative vapor phase chromatography is shown in Fig. 1.

Sample Injection Systems

Gases. Gaseous samples are drawn into the large motor-driven syringe *A*, through the sample gas inlet, *B*. The syringe is composed of a 3-inch diame-

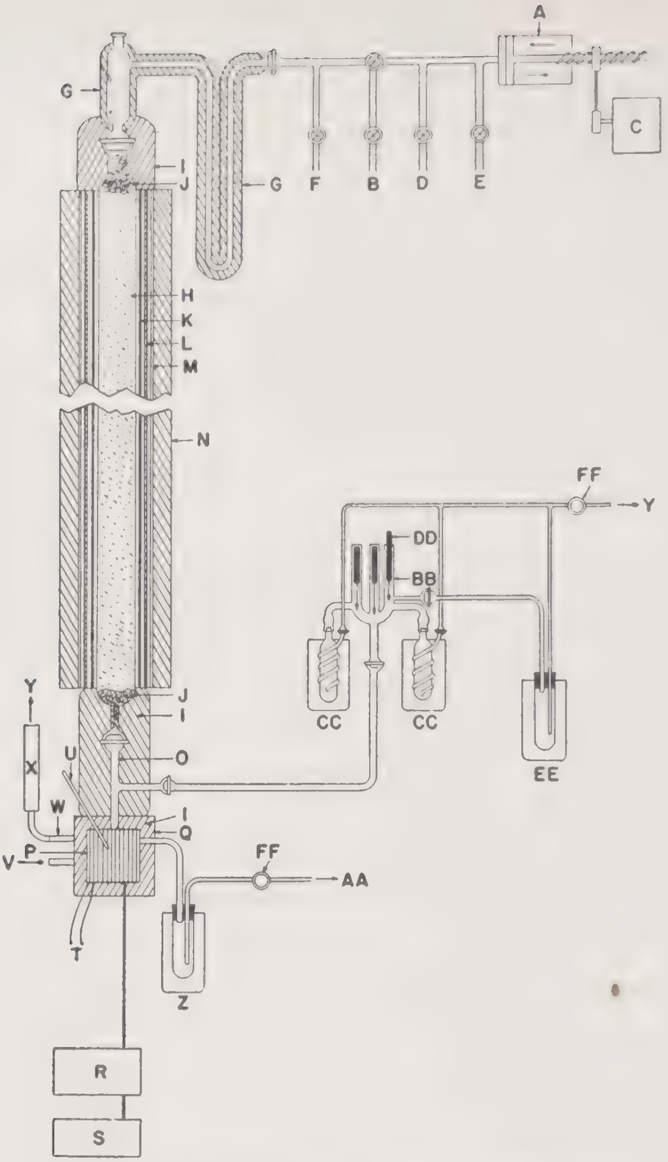

FIG. 1. Schematic of preparative-scale apparatus.

A. Motor driven "Teflon" syringe
B. Sample gas inlet
C. Motor
D. Vacuum pump connection
E. Manometer outlet
F. Metered, regulated carrier gas supply
G. Preheater-vaporizer (see Fig. 2 for details)
H. Packed glass column, 31 mm id
I. Fiberglass insulation
J. Glass wool plugs
K. Aluminum tubing, 1¾ in. od, 1.2 mm walls
L. Flat Nichrome wire heater on 51 mm od, 2 mm wall glass tubing
M. 64 mm od, 2 mm wall, glass tubing
N. Asbestos pipe insulation
O. Stainless steel "T" with 18/9 stainless steel inner spherical joints
P. Detector
Q. Transite detector box
R. Detector bridge (see Fig. 3 for details)
S. Recording potentiometer
T. Detector heater
U. Thermometer or thermocouple
V. Reference gas inlet
W. Reference gas outlet
X. Reference gas rotometer
Y. Vent
Z. Monitor stream cold trap
AA. Monitor stream rotometer and vent
BB. Sample trap manifold (see Fig. 4 for details)
CC. Sample cold traps (see Fig. 5 for details)
DD. Bar magnet
EE. Vent cold trap
FF. Needle valves

ter Teflon* fluorocarbon resin cylinder approximately 12 inches long, and a Teflon plunger which is close-fitted to the cylinder wall by means of a neoprene rubber "O" ring. The plunger is driven in or out of the cylinder by means of a screw-drive which is powered with a reversible motor, *C*. Limiting micro switches placed at appropriate positions on the screw-driving shaft permit automatic operation of the motor-driven plunger without danger of syringe damage. The gaseous sample is most easily introduced by evacuating the vacuum-tight cylinder in the withdrawn position by means of a vacuum pump attached to connection, *D*. The pressure in the cylinder is determined by a manometer attached to outlet, *E*. After introducing the sample into the cylinder, the manometer is closed off, the three-way stopcock leading to the column is opened, and, simultaneously, the cylinder plunger is driven in. The sample is then developed on the column by a metered, regulated carrier gas supplied from inlet, *F*.

Liquids. Liquids are vaporized before introduction on to the column, through the use of the preheater-vaporizer, *G*. This unit is detailed in Fig. 2. The sample is introduced through a rubber serum cap, *a*, at the top of the vaporizer unit. The vaporizer chamber, *b*, is filled with 1/8 in. stainless steel balls or glass beads, or glass helices, *c*, to facilitate the vaporization process. A two foot-long loop of heated glass tubing, *d*, precedes the vaporizer unit in order to preheat the carrier gas for rapid volatilization of the liquid sample. The temperature of the vaporizer is determined by an iron-constantan thermocouple, which is placed inside a small well, *e*, extending down into the vaporizer bed. The entire preheater-vaporizer unit is insulated with asbestos tape, *f*, and is heated by means of flat nichrome heating wire, *g*, whose power output is controlled by a Variac attached to power inlet, *h*. The preheater-vaporizer unit is connected to the sample inlet system and to the column through securely clamped spherical joints, *i* and *j*, respectively. When greased with a high melting silicone grease, these spherical joints maintain at least 15 psi pressure without leakage.

Column

Straight columns have been employed in this apparatus for purposes of convenience and economy. The columns, *H*, consist of glass tubing, six feet long and 31 mm I.D. The top of the column is connected to the vaporizer by means of a 35 mm spherical joint. This joint is insulated with Fiberglas insulation, *I*, in order to prevent condensation of the vaporized sample before it reaches the column. The column is fitted with glass wool retainer plugs, *J*, at the top and bottom of the column packing material. The temperature of the column is controlled by means of an electric heater surrounding the column. The heating unit is composed of an inner jacket of aluminum tubing, *K*, which is inside the flat nichrome heater, *L*, wound on glass tubing. The aluminum shell around the column insures even heating without "hot-spots". The nichrome heater itself is surrounded by a jacket of glass tubing, *M*, and the entire heater is insulated by means of asbestos pipe insulation, *N*. The columns can be heated to at least 250°C

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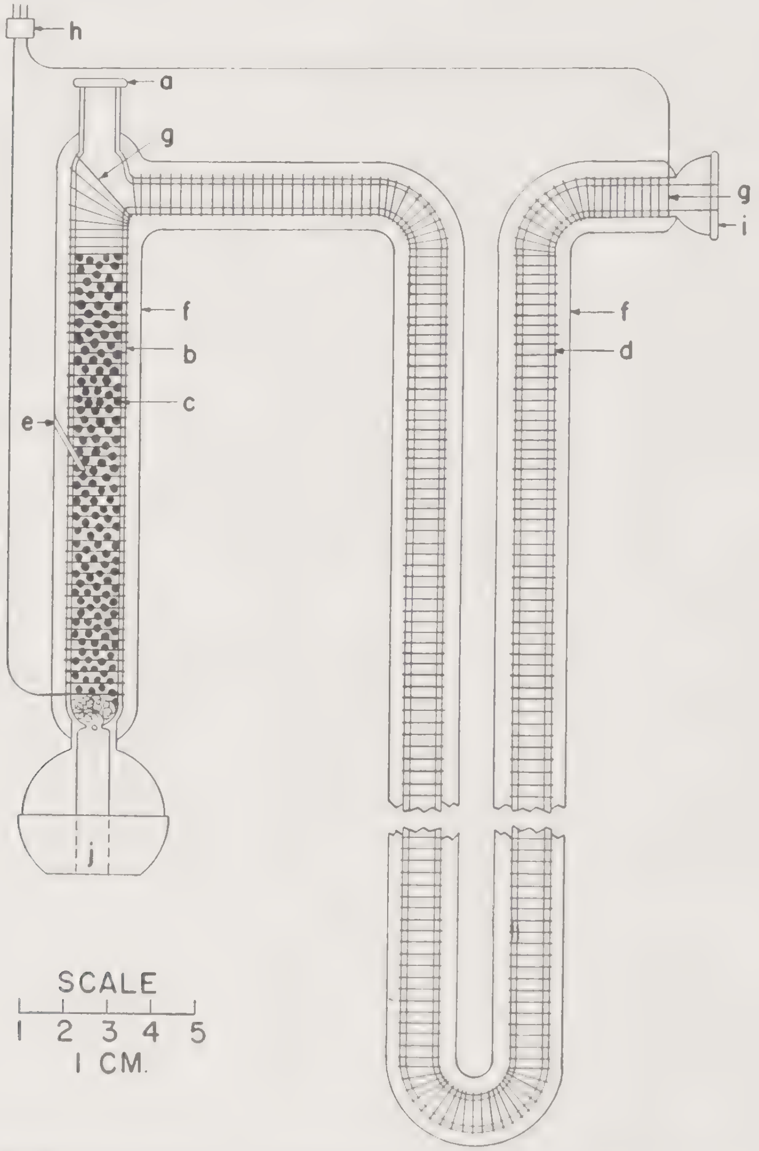

FIG. 2. Preheater-vaporizer. *a*. rubber serum cap; *b*. vaporizer chamber, 12 mm od glass tubing; *c*. ⅛ in. diameter stainless steel balls or glass helices; *d*. preheater, 9 mm od glass tubing; *e*. thermocouple well; *f*. asbestos tape insulation; *g*. nichrome heating wire; *h*. heater power inlet; *i*. gas inlet, 18/9 outer spherical joint; *j*. column connector, 35/20 inner spherical joint.

and require approximately 4 hours to reach this temperature, starting from room temperature. The temperature of the columns is observed by means of thermocouples inserted inside the aluminum shell at the top and bottom of the column. The column exit is connected to a stainless steel "T", *O*, with an 18 mm spherical joint. This "T" divides the column effluent into two streams, the main portion going to the trapping system, and a much smaller quantity of effluent passing into the detector which monitors the column output. The bottom of the column and the metal "T" are surrounded with Fiberglas insulation, *I*, in order to prevent condensation of the sample. During the separation of high boiling materials, it is desirable to heat this metal "T" with a heating tape in order to prevent condensation and hold-up of sample.

The apparatus is arranged so that more than one column may be placed in series in order to permit separations requiring more than 6 feet of column. The columns are connected by means of small "U" tubes which can be heated with electrical tape to prevent sample condensation between the columns.

The diameter of the column used in this apparatus was arbitrarily selected so as to permit the separation of large sample sizes with a reasonable degree of efficiency. The length of the columns was chosen as 6 feet for convenience of mounting in a still-rack. Use of spherical joint fittings on the column and its connecting units permits the quick interchange of columns when required. Replacement of a column can usually be carried out in about 10–15 minutes.

Detector

A Gow-Mac thermal conductivity cell, Model 9285 (Gow-Mac Instrument Company, Madison, New Jersey), was used as detector in the apparatus. This unit consists of a stainless steel block, *P*, housing four tungsten sensing filaments. The detector block is securely suspended in a Transite box, *Q*, approximately 5 × 5 × 5 in. Fiberglas insulation, *I*, was packed between the detector block and the box. The sensing elements were wired into a detector circuit, *R*, detailed in Fig. 3, in such a manner that two of the cells were in series for the reference gas flow and two of the cells were in series for the sample gas flow. This arrangement results in good sensitivity and linearity of the detection system (*5*). A Brown recording potentiometer, *S*, of 2.5 millivolts sensitivity was used to record the output from the bridge circuit. The thermal conductivity cell is heated by an insulated heating wire, *T*, of approximately 25 ohms, wound directly on the metal block. The power to this heater, supplied through leads, *T*, was furnished by a 24 volt, one ampere filament transformer. The temperature of the detector was controlled by varying the input voltage to the

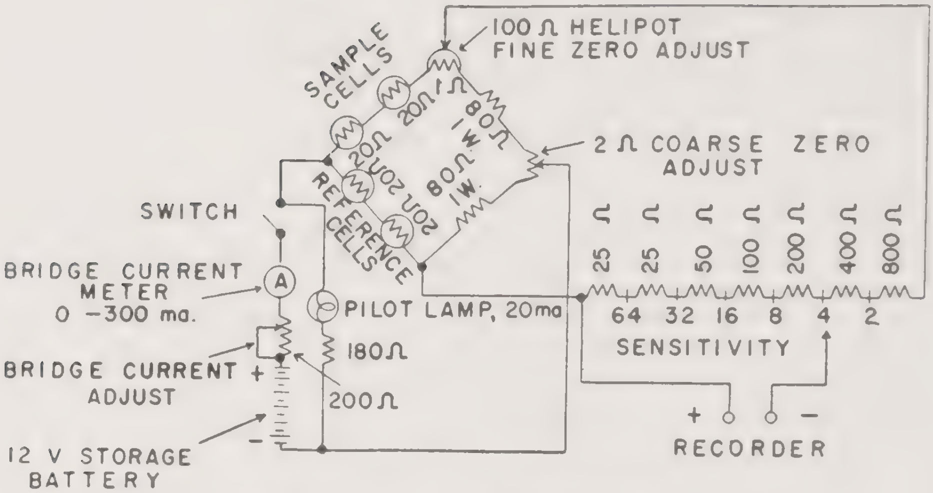

FIG. 3. Detector bridge schematic.

filament transformer by means of a Variac. A thermometer or thermocouple, *U*, was used to observe the temperature.

The gas flow pattern in the detector cell was such that the reference carrier gas was passed slowly into inlet, *V*, over the reference filaments, and venting at *W*. The rate of reference gas flow was measured with a rotameter, *X*, and then passed into vent, *Y*. The monitored portion of the sample gas stream enters the detector from the metal "T", *O*, passes over the sample filaments, and then flows through a cold trap, *Z*. This trap retains vapors that might otherwise condense in a rotameter which is attached at position, *AA*.

Trapping System

Desired portions of the chromatographic effluent are trapped by means of a special glass apparatus consisting of a trap manifold, *BB*, and sample cold traps, *CC*, shown in detail in Fig. 4 and 5, respectively. The use of the trapping system is most readily explained by reference to Fig. 4. The sample stream enters at inlet, *k*, and passes into a low-volume chamber from which three outlets, *l* and *m*, are attached. All three outlets are controlled by special Teflon valves (*9*) which consist of Teflon cone-plugs, *n*, which fit into 30° glass seats, *o*. The Teflon plugs are attached to magnetic bars, *p*, by means of tungsten wire, *q*, coupled to a platinum tube, *r*, by a spot-weld, *s*, and held by a platinum pin, *t*. The plugs can be raised by placing a small external magnet (*DD*, in Fig. 1) placed at the top of the posts containing the valve to be activated. The attraction of the magnetic bar, *m*, attached to the Teflon plug, causes the valve to open. The valve is closed by removing the external magnet. In operation, the vent valve, *m*, is kept in the open position (external magnet in place) until the trapping is to commence. At the moment that a peak is to be isolated, the magnet from the vent valve is removed, and, simultaneously, a magnet is placed on top of either of the valves, *l*, controlling the sample traps. After collecting the desired sample in the trap connected at *u*, the operation is reversed to again divert the chromatographic stream back to vent, *v*.

The cold traps, *CC*, in Fig. 1, used with the sample collection unit are of

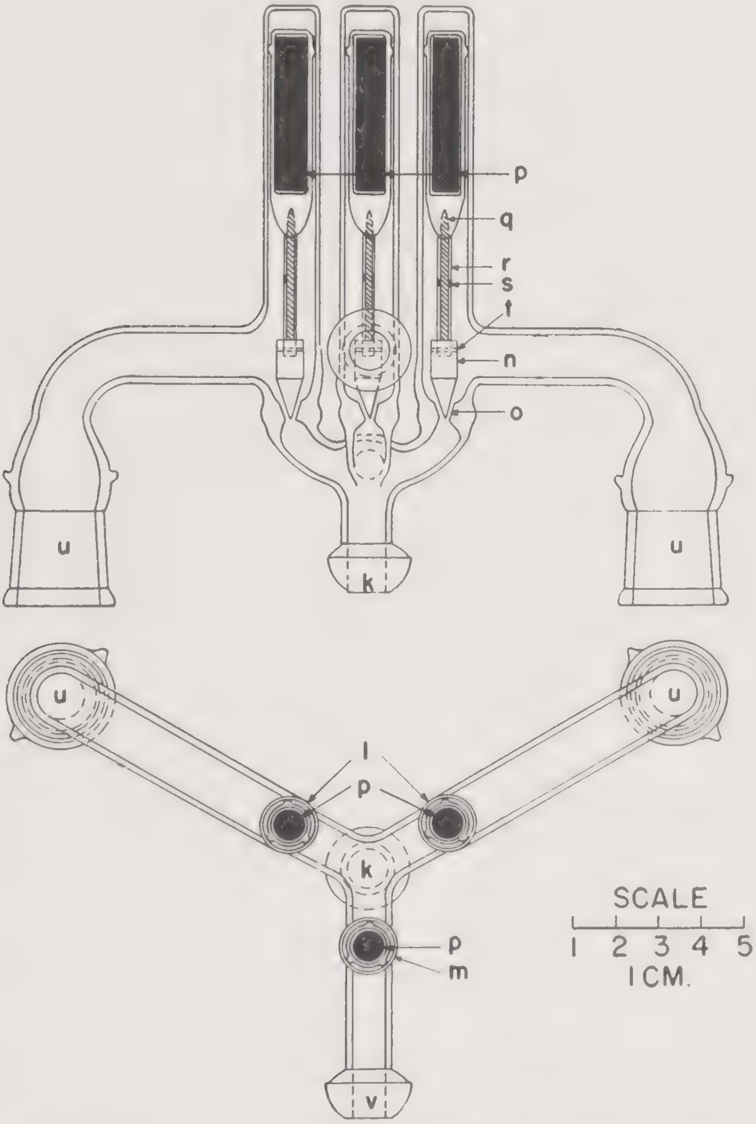

FIG. 4. Trap manifold. *k*. column effluent inlet, 18/9 inner spherical joint; *l*. trap valves; *m*. vent valve; *n*. 30° angle "Teflon" plug; *o*. valve seat; *p*. ¼ in. diameter polarized magnetic bar; *q*. 0.040 in. od tungsten wire; *r*. 0.058 in. od, 0.042 in. id platinum tubing; *s*. spot weld; *t*. platinum pin; *u*. trap connector, S/T 19/22 outer joint; *v*. manifold vent outlet, 18/9 inner spherical joint.

an efficient, spiral design shown in detail in Fig. 5. The chromatographic stream enters at the top of the trap via a standard taper inner joint, *w*. The vapors must pass down the tube past the cold wall filled with 1/4″ deep indentations, *x*. The stream then passes through a glass spiral coiled about the trap, and exits through the spherical glass joint, *y*, which connects to the vent system. Liquid condensates collect in the bottom reservoir which holds 10–12 ml, thus permitting the collection of at least this amount without pluggage of the trap. Similar traps have been constructed with 25 ml reservoirs for use with larger samples or multiple isolations.

The cold trap, *EE*, shown in Fig. 1, is an optional vent trap employed

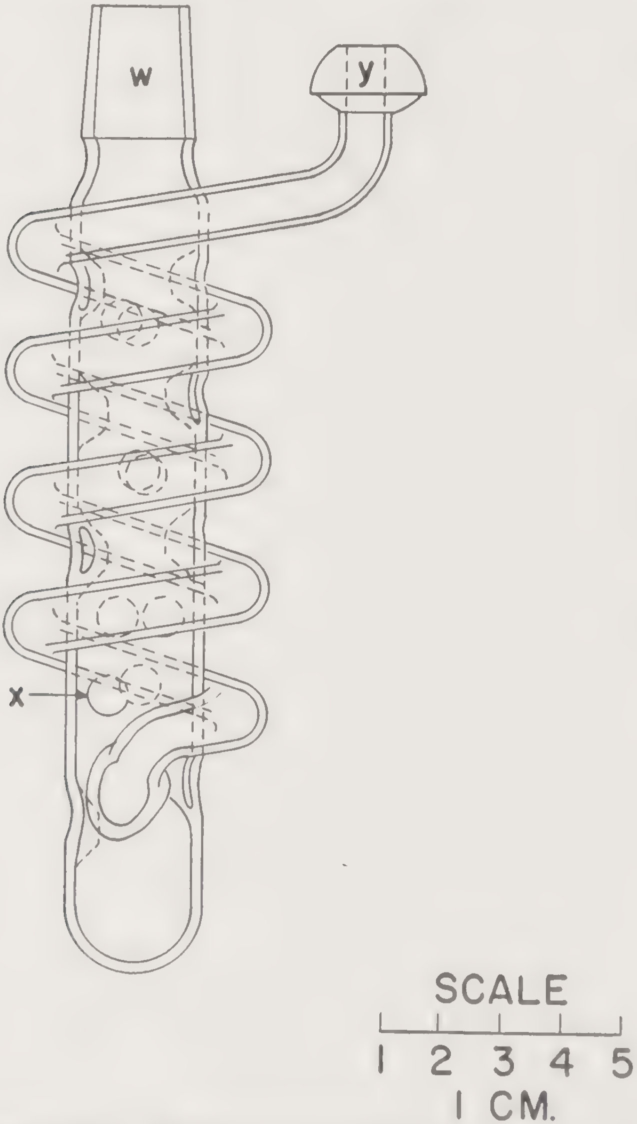

FIG. 5. *Sample Trap*. *w*. 19/22 S/T inner joint; *x*. 1/4 in. deep indentations; *y*. 18/9 inner glass spherical joint.

to prevent condensable waste fractions from collecting in the vent line, which might disturb the flow of the column effluent.

In order to establish the proper flow of the column effluent into the monitoring cell, the trap vent lines and the manifold vent line are collected into a common line in which a needle valve, *FF*, is placed. By adjusting the flow through this valve and through a similar valve in the monitor stream outlet, the desired flow rate may be obtained, as indicated by a rotameter attached to *AA*.

OPERATION

Sample Injection

In order to insure optimum chromatographic performance, it is desirable to introduce the sample into the column as quickly as possible, so as to obtain a relatively narrow initial band-front. Introduction of a large volume of gaseous sample by displacement of the sampling tube volume with the carrier gas results in poor resolution due to the non-instantaneous introduction of the sample into the column (*10*). With this technique, the sample is carried on to the column over a period of time due to the exponential mixing in the sampling tube, and the chromatogram produced will be a superposition of a number of chromatograms, whose origins vary over the time taken for the sample to be introduced. The effect is particularly important when attempting separation of gases on a large scale. This sampling difficulty is overcome, however, by using the motor-driven syringe system described above. Approximately 500 cc of a gaseous sample at atmospheric pressure can be introduced onto the column in about seven seconds, which results in a sharp initial sample band with accompanying good chromatographic resolution.

In order to insure rapid introduction of liquid samples onto the large-scale chromatographic column, an efficient sample vaporizer should be employed. The temperature of the preheater-vaporizer unit used during this study was normally maintained at least 50–75°C above the boiling point of the highest boiling material in the mixture to be separated. In the case of very large sample charges (10 cc), it has been found necessary to increase the temperature of the vaporizer as much as 100–150°C above the sample boiling point, in order to insure instantaneous volatilization during injection of the entire liquid sample. (The same effect could undoubtedly be obtained at a lower temperature by using a larger vaporizer of higher heat capacity.) When the vaporizer temperature has been properly adjusted, 10 cc of liquid sample may be injected in 5–7 seconds with instantaneous vaporization.

For the introduction of liquid samples when two columns are used in series, an inverted version of the preheater-vaporizer shown in Fig. 2 has been used. In this case, the sample is injected at the bottom of the first column, the vapors pass up the column, through a low-volume connecting "U"-tube and down the second column into the trapping system and monitoring detector. The upright vaporizer is again used when three columns are employed in series, since the arrangement is in the form of an "N", with sample injection again carried out at the top of the first column.

Low-melting solids may be melted and injected into the vaporizer as liquids.

Operation of Column

Several different packings were used in the large-scale columns employed during this investigation. Celite 545 is the preferred solid supporting material for separating samples containing a variety of types of compounds, since this material can be more easily modified than can other types of supports such as crushed firebrick, calcined Celite, or Florisil. When separating highly polar compounds which normally tend to adsorb on the substrate, it has been found desirable to "deactivate" the Celite before coating it with the proper organic liquid. In these instances, the Celite is prepared by first sieving out a 60–80 mesh fraction, slurrying it with concentrated hydrochloric acid to remove acid-soluble impurities, filtering, and washing the wet material with distilled water until it is acid-free. This acid-washed material is then slurried with 1 *N* aqueous sodium hydroxide and permitted to stand for at least 30 minutes. Following this treatment, the resulting treated Celite is filtered off and dried without washing in a 120°C oven for 48 hours.

The columns used in the apparatus herein described contain packing material which consisted of 25%, by weight, of the liquid phase employed. Approximately a kilogram of packing material is required to fill a column of the dimensions described above. The liquids were deposited on the solid substrate by slurrying with a suitable low boiling solvent and evaporating the solvent. The resulting dry material was packed into the glass columns by means of vibration. Columns containing adsorbents, such as activated charcoal and silica gel, were packed in a similar manner.

The liquid phase employed in the column packing is entirely dependent on the type of separation which is desired. Selection of the proper liquid is most easily accomplished by "piloting" the separation on analytical-scale apparatus. During the present study pilot runs were carried out on a modified Perkin-Elmer Model 154-B Vapor Fractometer, using $^{3}/_{16}$″ I.D. stainless steel columns 2 meters long. In a large-scale separation, the relative positions of the various peaks, compared against that of a suitable internal standard, can usually be predicted with good accuracy from an analytical-scale pilot run, provided comparable operation conditions are employed.

The volatility of the stationary liquid phase is more critical with large-scale separations, than with semi-micro analytical applications. A particular liquid phase which gives satisfactory analyses on an analytical scale might prove to be too volatile for large-scale work, as evidenced by the contamination of the isolated fraction by the liquid phase, or its degradation products. In general, it appears desirable to use the liquid phase at no higher temperature than about 200°C below its boiling point. High-boiling esters, such as dibenzyl sebacate and di-*n*-decylphthalate can usually be safely operated up to about 140–150°C without undue contamination. The most temperature-stable liquid phases found to date are high-vacuum silicone grease treated in the manner described by Cropper and Heywood (*3*) and Apiezon L high vacuum grease. The former material has been used up to 225°C without difficulties due to volatility or decomposition; however, the upper temperature limit for this substance has not yet been established.

Helium has been used as the carrier gas for most of the separations carried out to date, since this gas permits the detector to respond with high sensitivity. Nitrogen can also be used satisfactorily as a carrier; however, this results in a significant lowering of the sensitivity of the detector. Hydrogen has not been used with this apparatus because of safety considerations, but presumably could be employed successfully.

The rate of carrier gas flow needed for a desired large-scale separation may often be satisfactorily estimated by multiplying the flow rate found on an acceptable analytical-scale separation, by the ratio of the internal areas of the two columns.

Most of the separations carried out on the large-scale apparatus have been made using carrier gas flow rates of 1.5 to 4 liters per minute. A carrier gas input pressure of about 5 psi is required to furnish a column flow rate of approximately 3 liters per minute helium for a 6-foot column, using packing material described above. When several columns are to be connected in series, it is often desirable to use column packing containing 35–60 mesh solid substrate in order to keep the overall pressure drop of the column as low as possible.

The amount of sample that may be charged to a column is dependent on the nature of the materials in the mixture and on the chromatographic technique used. An average charge to a 6-ft column appears to be about 2 g; a difficult separation may limit the charge to one-fourth this amount. If the peaks are widely separated, it is possible to deliberately overload the column with as much as 10–15 g. Inability to carry out a particular isolation due to overlapping of peaks may often be solved by operating at a lower temperature than would normally be used for a routine analytical

TABLE I

Comparison of Column Efficiencies

Peak Measured	Column Packing	Temp., °C	Theoretical Plate Nos. (4) per centimeter of column	
			Analytical	Large-scale
Trimethylamine (in commercial dimethylamine)	Carbowax 400 on base treated Celite 545.	50	3.2	4.1
Impurity (in practical grade *p*-methoxyacetophenone)	Silicone grease on crushed firebrick	185	2.6	2.6
Dichlorobenzoic acid, methyl ester	Silicone grease on crushed firebrick	225	1.7	1.4

separation. Increasing the column length also permits the use of correspondingly larger sample sizes. For instance, if it is found that a 2 g charge is maximum for a 6-ft column, and still permit the desired separation, then an 18-ft column will handle a 4–6 g charge with equivalent efficiency. As indicated previously, the ability of the vaporizer to volatilize liquid samples instantaneously also has a profound influence on the quantity of sample which might be charged to a column for a particular separation.

The effect of increasing the column diameter on the column efficiency has not been studied in detail; however, data obtained on a limited number of systems indicate that there is no difference between the efficiency of a 4.75 mm id column and a 31 mm id size using comparable operating conditions, as shown in Table I.

Monitor Operation

The thermal conductivity cell was operated in conformance to directions suggested by the manufacturer. The bridge current was maintained at 175–200 ma when using helium as the carrier gas, and 125–135 ma when nitrogen was employed. The sample stream flow-rate through the monitor cell was held at about 40 cc/min during the study. Since the "dead volume" of the trapping system is relatively small, the time required for a component leaving the column to reach the trapping system is about 3–4 seconds, which is also approximately the time required for the component to be sensed by the detector.

The temperature of the detector should be set at the temperature of the column, or slightly higher, so that no component of the sample can condense in it during a run. Excessively high detector temperatures should be avoided because of decreased detector sensitivity and stability.

In order to be able to detect very minor components which might lie close to the peak to be trapped, most large-scale runs were carried out at a high detector sensitivity. This technique gives a better indication of when the trap should be introduced and disconnected, and, as a result, enhances the possibilities of obtaining a pure fraction.

Isolation Techniques

Liquid nitrogen, Dry Ice-acetone, brine, and wet ice have all been used satisfactorily as trap coolants. Selection of one of these should be governed by the volatility of the material to be isolated. Although Dry Ice-acetone mixtures will cool the traps sufficiently to condense the large majority of materials normally encountered, some difficulty with trace contamination of the final trapped sample with acetone has been experienced. Care should be taken that air from the vent line is not permitted to be drawn into traps cooled in liquid nitrogen due to condensation of the oxygen in the air.

The spiral traps used during this investigation have been found to be extremely effective, even for materials which are difficult to condense, such as low boiling gases, and high boiling compounds which tend to form "fogs" when cooled rapidly. Most trapping operations can be made to be essentially quantitative, and even difficultly-condensable materials are usually collected with an efficiency of better than 80% at flow rates of 4 liters per minute of carrier gas. Since the manifold-trapping system has a relatively small "dead-volume", no mixing takes place between fractions which have been completely separated chromatographically.

When using the trapping device with readily-condensable compounds, it may become necessary to warm the connecting lines and the manifold to prevent condensation of the fraction. This is readily accomplished by wrapping the system with an electrical heating tape whose power output is controlled by a Variac. Application of heat to the manifold in no way hampers the operation of the valves up to temperatures as high as 200°C.

With the type of trapping system described herein, it is possible to trap two successive peaks with no delay or interruption of the chromatographic process. By connecting two or more manifold-trap systems in series, it is possible to collect as many fractions as desired during a single chromatographic run. Although operation of the traps has been confined to manual operation in this investigation, it would be relatively simple to operate the valves with solenoids operated by switches, instead of magnets. This refinement, coupled with a timing mechanism, would make collection of fractions an automatic process.

APPLICATIONS

Large-scale vapor phase chromatography is an important analytical tool for isolating unknown materials from very complex mixtures in sufficient quantities for subsequent characterization by both physical and chemical methods. Preparation of pure samples for use as analytical standards and for biological testing represent other valuable uses. The apparatus described in this paper has been satisfactorily employed in investigations which necessitated the handling of materials of highly variant chemical composition and physical characteristics. In order to demonstrate the versatility of the equipment, a few of these studies are described in the following sections.

Purification of n-Butanol and Identification of Minor Impurity

n-Butanol is difficult to obtain in very high purity by fractional distilla-

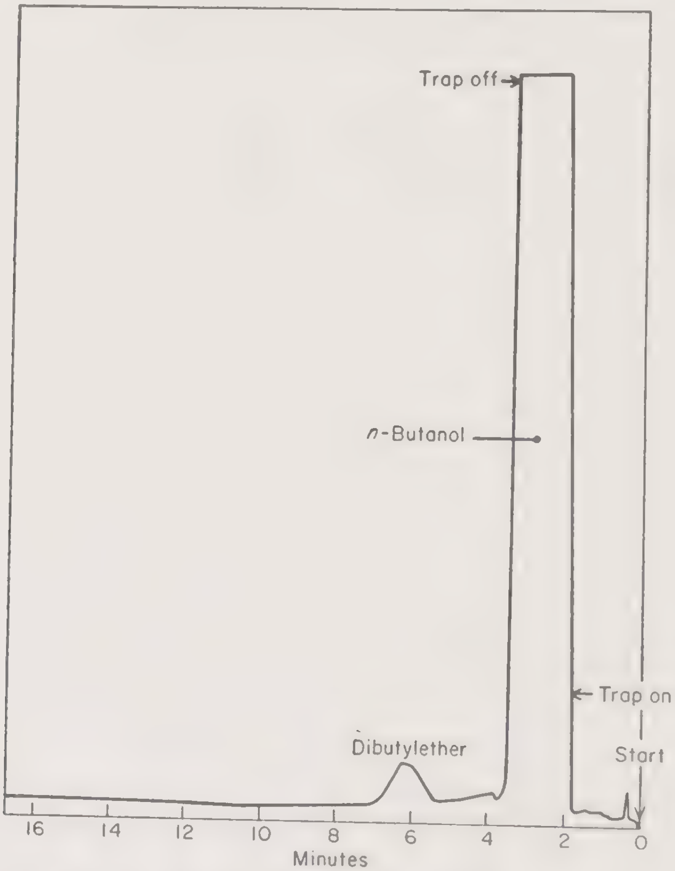

FIG. 6. Preparative-scale isolation of *n*-butanol and impurity.
Column—6 ft × 31 mm di-*n*-decylphthalate on Celite
Temperature—115°C
Flow—2100 cc/min He
Sample—2 cc

tion because of the close-boiling azeotropes that are formed with the small amounts of water and minor organic impurities present. Using the large-scale VPC apparatus, highly purified *n*-butanol may be prepared in significant quantities in a run requiring no more than 10 minutes. A preparative run is shown in Fig. 6, in which a 2 cc sample of CP *n*-butanol was injected on to a 6-ft column of di-*n*-decylphthalate supported on 60–80 mesh Celite 545. The separation was carried out at 115°C with a helium carrier gas flow of 2100 cc/min. A comparison of the quality of the original CP *n*-butanol and the resulting purified sample was obtained by analyzing these materials at high sensitivity on a Perkin-Elmer Model 154-B Vapor Fractometer analytical VPC instrument. The results are shown in Fig. 7; the upper curve in Fig. 7 shows the original CP sample, and the lower curve

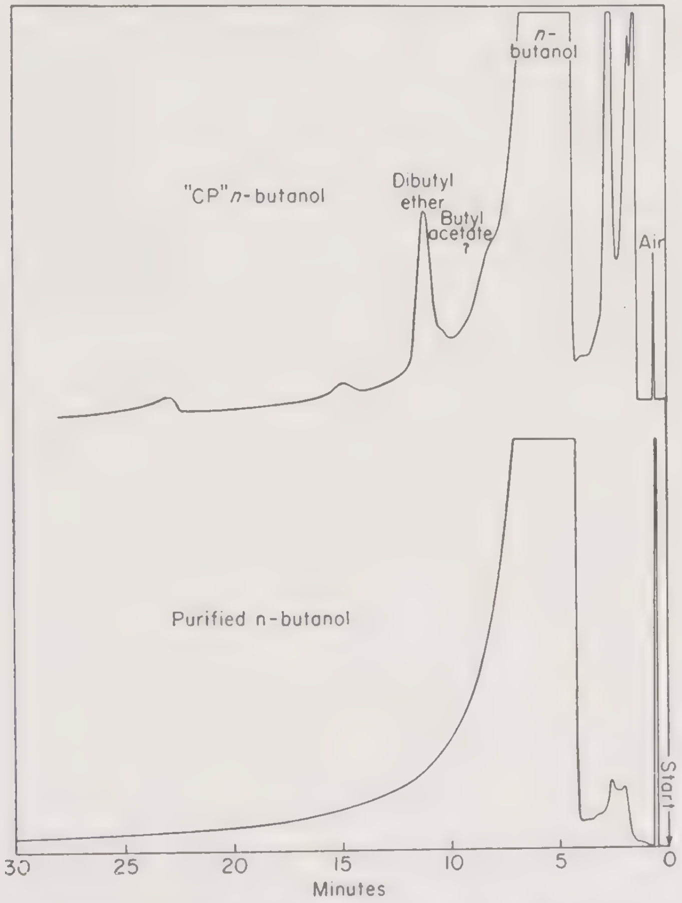

FIG. 7. Comparative analysis of CP and chromatographically purified *n*-butanol.

Column—2 meter-di-*n*-decyl phthalate on Celite
Temperature—115°C
Flow—46 cc/min He
Sample—50 μl

the same material after purification. Only a very small amount of water (probably contamination during handling) and two other trace low-boiling impurities were noted in the purified sample. The total of these known impurities has been estimated at no more than 0.07%.

Unknown components occurring in a mixture in very low concentrations may be isolated by the large-scale apparatus and identified by means of a suitable secondary detector. An example of this is the positive identification of the impurity emerging at about 6 minutes in the separation shown in Fig. 6, which was carried out by trapping out this peak and analyzing it by infrared spectroscopy. Previous retention time data had indicated that the material might be di-*n*-butylether, and this was confirmed in the isolation experiment. Since the original material contained about 0.5% of this compound, approximately 8.5 mg was trapped for analysis. The identification was made by washing the trap out with 0.5 ml of carbon disulfide, and scanning the resulting solution in a Perkin-Elmer Model 21 infrared spectrophotometer using solvent compensation and ordinary technique.

It can be noted in the analysis of the highly purified *n*-butanol shown in Fig. 7 that no di-*n*-butyl ether was detected. The limit of sensitivity for this compound under the conditions of the analysis is about 50 ppm.

Purification of Dimethylamine

In order to obtain an analytical reference sample of dimethylamine, commercial material was purified by large-scale VPC. A cylinder of CP dimethylamine was first analyzed by VPC and found to contain about 0.75% trimethylamine, smaller amounts of monomethylamine, an unidentified trace impurity, and a very small amount of ammonia. Approximately 500 cc of this starting material at 700 mm pressure was injected into the chromatographic column using the large motorized Teflon syringe described previously. The sample was chromatographed on a 6 ft, 31 mm I.D. column of Carbowax 400 (polyethylene glycol) supported on 60–80 mesh Celite 545. The column was operated at 50°C with a helium carrier gas flow rate of 2750 cc/min. The large-scale separation is shown in Fig. 8. The dimethylamine peak was isolated in a liquid nitrogen cold trap, volatilized, and transferred to an evacuated gas bulb. Comparative VPC analyses of the original CP dimethylamine and the VPC-purified material shown in Fig. 9 clearly demonstrates the effectiveness of the purification. No trimethylamine was detected in the sample when analyzed at the highest instrumental sensitivity available. A very small ammonia peak was seen (less than 25 ppm), but this contamination is believed to be due to partial adsorption of this material on the glass surface of the manifold during the

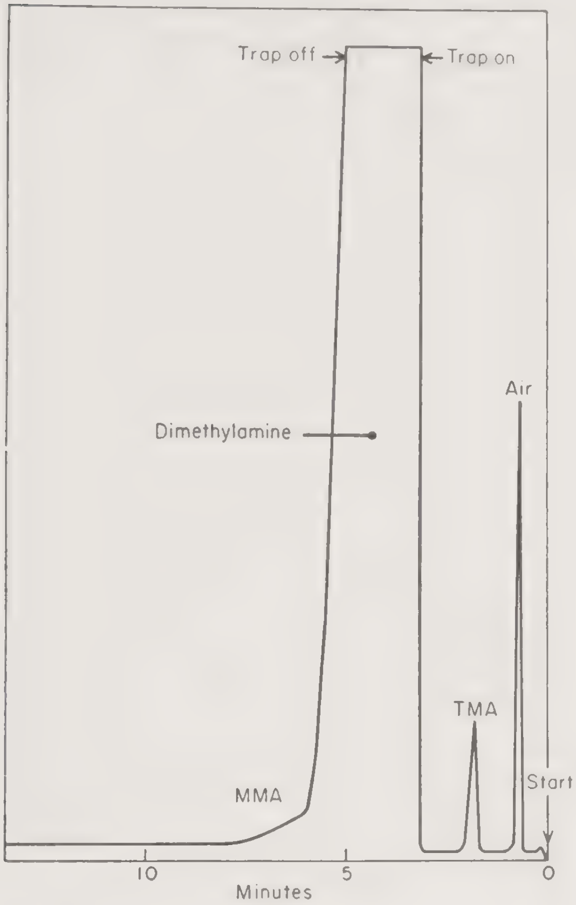

FIG. 8. Large-scale isolation of dimethylamine.
Column—6 ft × 31 mm I.D. Carbowax 400 on Celite
Temperature—50°C
Flow—2750 cc/min He
Sample—500 cc at 700 mm.

separation and release at the taking of the next fraction, since the compound was completely separated chromatographically. The air peak shown in both separations in Fig. 9 was caused by contamination during the analytical sampling process.

Although the compound separated and trapped in this study boils at 7°C, the large-scale equipment can be used for the isolation of components boiling much lower by employing suitable column packing material and trap coolants. Very volatile materials can be retained by filling the cold traps with activated alumina, activated charcoal, or molecular sieve. The adsorbed components can be recovered by distilling at reduced pressure into another empty cold trap immersed in liquid nitrogen.

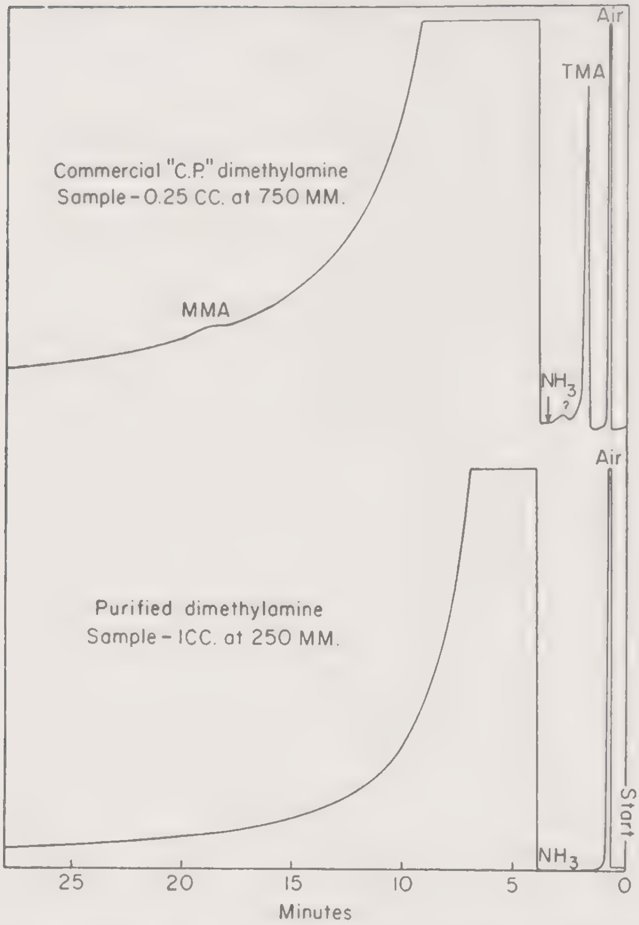

FIG. 9. Comparative analysis of CP and chromatographically purified dimethylamine

Column—2 meter Carbowax 400 on Celite
Temperature—50°C
Flow—42 cc/min. He

Isolation of Purified p-Methoxyacetophenone

Low-melting solids can also be purified by large-scale VPC, providing the material is sufficiently volatile and is reasonably stable at the operating temperatures employed.

Practical grade *p*-methoxyacetophenone contains three close-boiling minor impurities which are difficult to eliminate by fractional distillation or crystallization. Purified *p*-methoxyacetophenone (bp 258°C, mp 39°C) was obtained by chromatographing one cc of melted practical material through a 6 ft large-scale column packed with silicone grease on crushed firebrick. The column was operated at 188°C with a helium carrier gas flow of 2900 cc/min, and a vaporizer temperature of 268°C. Fig. 10 gives a

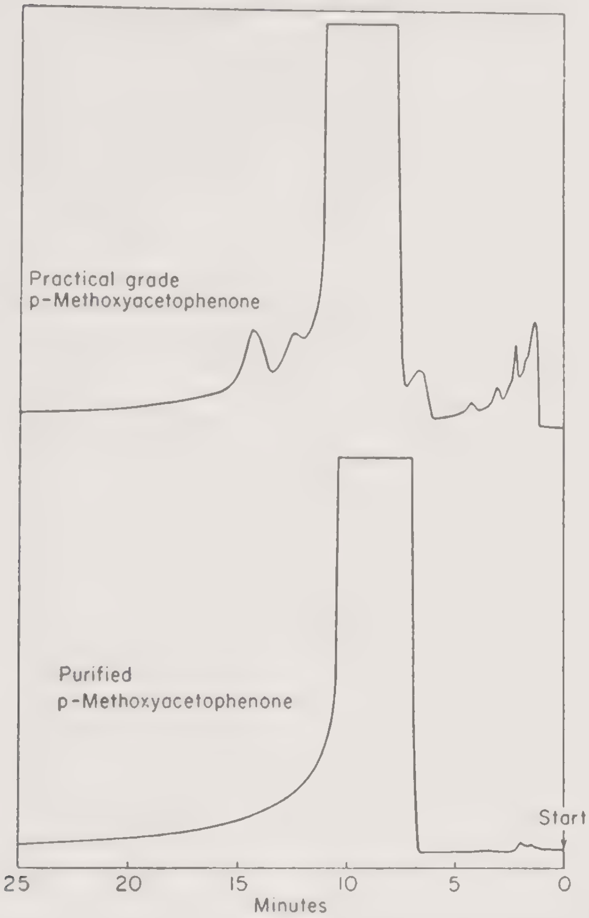

FIG. 10. Analysis of p-methoxyacetophenone before and after purification by large-scale vapor phase chromatography.

Column—2 meter silicone grease on firebrick
Temperature—185°C
Flow—50 cc/min He
Sample—25 μl

comparison of the p-methoxyacetophenone before and after purification, as found by high-sensitivity VPC analysis.

Acknowledgment

The author is indebted to R. G. Nester, Central Research Department, E. I. du Pont de Nemours & Co., Inc., for assistance in designing the trapping system described in this paper.

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CHAPTER XXII

Isolation and Identification of a Low Concentration Component by Gas Chromatography and Mass Spectrometry

RALPH E. RIPPERE

General Engineering Laboratory, General Electric Company, Schenectady, N. Y.

As part of an organic reaction study, an identification of a predicted product was required. The actual reaction mixture submitted contained no more than 0.02 mole per cent of a possible product, which was comparable in volatility to the starting material.

The separation of the starting material, benzene, and the anticipated possible reaction products 1,4- and 1,3-cyclohexadiene, cyclohexene, and cyclohexane had been shown to be possible, in earlier work, on a gas chromatography column packed with fluorene and picric acid on Celite (12.5:12.5:75). Favorable conditions were a 4-meter column, 100°C, and 60 ml of helium per minute through ¼″ ID column. The components of a synthetic mixture exited in the order cyclohexane, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, and finally benzene.*

In process control gas chromatography examinations showed that the starting benzene contained some .05 mole per cent of cyclohexene and cyclohexane. During the reaction, bands appeared and slowly increased in intensity indicating the progressive production of 1,4- and 1,3-cyclohexadiene. These bands increased to indicate a maximum of 0.02 mole per cent of the 1,4-material, compared to the area of the 0.05 mole per cent initial impurities. Because of equipment limitations, the reaction could not be continued beyond this point to increase the concentrations of the components of interest.

The chromatography sample of 50 μl was within the capacity of the column, at the conditions cited. Thus, for one pass, approximately 8 μg of 1,4-cyclohexadiene could be obtained, and less, probably 2 to 3 μg of the 1,3-isomer.

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*Compound	Source	b.p. (nom.)
benzene	E. Kodak Co.	80.1
1,4-cyclohexadiene	Farchan Res. Laboratories	85.5
1,3-cyclohexadiene	" " "	79–80
cyclohexene	E. Kodak Co.	83.3
cyclohexane	" " "	80.7

The sensitivity of an available commercial mass spectrometer was found adequate, at this level of sample, and accordingly was calibrated for fracture patterns of the five compounds of interest in the study.

The fracture patterns, or relative intensities of charged masses were obtained on the instrument just prior to the analytical determinations. These showed the degree of differentiation necessary to distinguish between the compounds. Four of these patterns are already available in the literature, the fifth was new.

A two-way valve and a diversion tube were fitted at the exit of the chromatography column to enable the separation of the helium carrying the component registering on the recorder at the time this was occurring. This diversion tube was connected by $\frac{1}{8}''$ flexible plastic tubing to a $3''$ portion of a hypodermic needle tube leading through a rubber stopper into a U-tube. This U-tube, 5 mm i.d., was valved to the atmosphere through an attached mercury trap, to minimize condensation of atmospheric moisture when immersed in liquid air to freeze out the hydrocarbon. Standard taper joints on the U-tube itself matched those on the mass spectrometer sample manifold. Trial runs, separating known two component mixtures demonstrated the workability of the diversion-trapping attachments to the gas chromatography instrument, and rehearsed the operator in the collection of the component in a selected band.

Finally two duplicate separation runs with diversion of the suspected 1,4-component were made and the frozen out fractions analyzed on the mass spectrometer. Close analyses were obtained applying the conventional method of linear simultaneous equations to the total pattern obtained on the mass spectrometer. These analyses showed:

5%	Benzene
83%	1,4-cyclohexadiene
12%	1,3-cyclohexadiene.

The presence of the small amounts of minor component is probably due to turbulence of the exit gases between the column exit and the diversion valve, for the 1,3-cyclohexadiene. The 1,4-cyclohexadiene appeared, at this low concentration level, as a side band at the start of the benzene band and hence could not be diverted without some benzene contamination. This contamination could be readily measured by the mass spectrometer.

Acknowledgment

The author is indebted to Mr. J. A. Hill for the gas chromatography and Mr. G. P. Schacher for the mass spectrometry.

Chapter XXIII

The Calculation of the Continuous Gas Chromatographic Column

Paul Benedek, Leslie Szepesy, and Stephen Szépe*

Hungarian Petroleum and Gas Research Institute, Veszprém, Hungary

The continuous gas chromatographic process (Hypersorption) developed by Berg (*1*) was investigated in connection with the separation of various gas mixtures. The results of these investigations were presented in part previously (*2*, *3*). This paper covers only the calculation of the rectification sections of these units in a few technological schemes. A detailed discussion of these methods (*4*) is not the purpose of the paper. The importance of adsorbent rate—which was neglected by others—is emphasized. A new separation scheme is presented (Scheme 2).

In all the schemes presented, the main parts of the column (Fig. 1) are the cooler, the separation section, and the desorber. The separation is accomplished by a moving bed of adsorbent (usually activated carbon), which is in continuous circulation by means of a pneumatic conveying system. The differences in the schemes are only in the separation sections, presented in Fig. 2. (On the figure the upper and lower parts of the rectification section are designated—according to the distillation analogy—as fractionating and stripping zones, resp.)

Scheme 1 represents the separation of a binary mixture. This method has less commercial interest, but this is the most suitable for the study of the process (especially of the rectification section). This scheme is the most easily calculated and, therefore, the outline of the calculation method will be illustrated by this one.

Schemes 2 and 3 are suitable for the separation of multicomponent gas mixtures, and they have considerable commercial importance. Scheme 2 can, for instance, be applied for the recovery of pure ethylene from cracked gases and Scheme 3 for the recovery of pure acetylene from the end gases of the partial oxidation of methane.

In Scheme 2, the gas to be recovered has a medium adsorbability and the lighter components can be regarded as a single inert. It employs a side stream of adsorbent, which is the upper part of the rectification section, for purification of a third product, taken off above feed.

As it is impossible to take off directly pure middle product from a distillation column, a middle product of a simple continuous gas chroma-

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* Present address: Sinclair Research Laboratories, Inc., Harvey, Illinois.

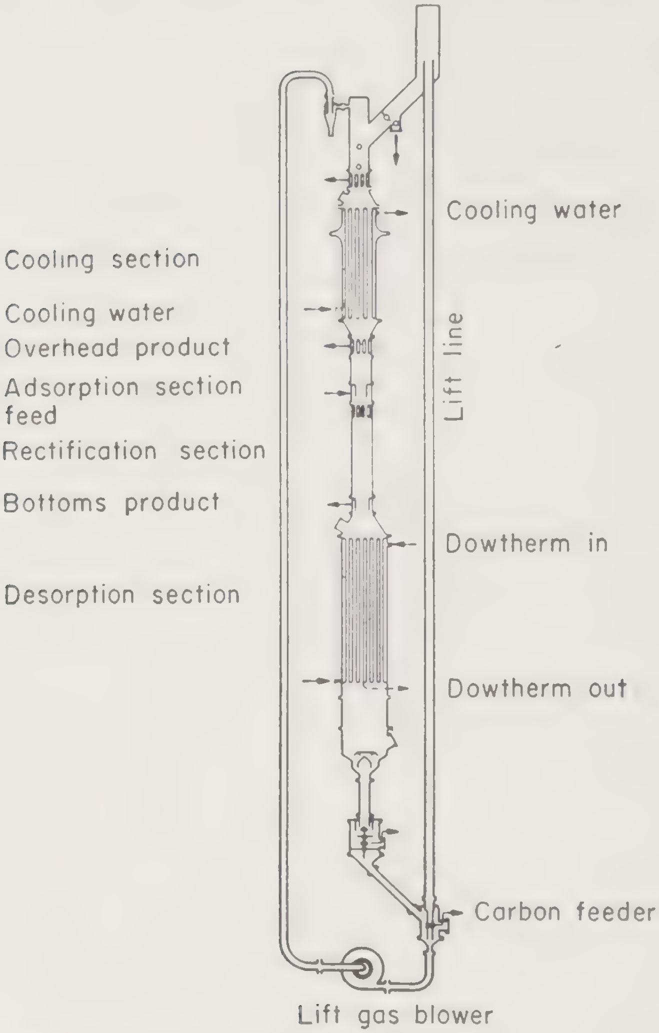

Fig. 1. Continuous gas chromatographic column.

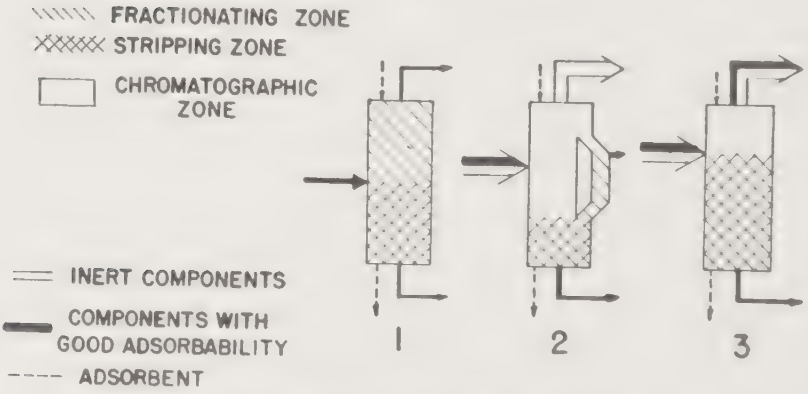

Fig. 2. The separation sections of the different schemes.

tographic unit always contains impurities and, therefore, further purification in a second unit or absorption column is necessary. However, with Scheme 2 it is possible to recover a middle product of any desired purity. In this case, the flow of the adsorbent is divided into two parts, one of them represents the frontal chromatographic (adsorption) section, and the other the rectification section. The middle product in this scheme is the overhead of the rectification section, in which a binary mixture is introduced in an adsorbed phase.

In Scheme 3 the gas to be recovered has the greatest adsorbability in a mixture which contains two components with considerable adsorbability (in the example: acetylene and carbon dioxide), while the other gases can be regarded as a single inert component.

In all these cases, the essence of the separation process is a counter-current phase exchange between an adsorbed and a gas phase. The process is, therefore, similar to distillative rectification, especially to extractive distillation. In the calculation of the process and in the design of the units the distillation analogy was used. The similarities and the differences of distillation and continuous gas chromatography will be illustrated in Scheme 1.

Because in continuous gas chromatography a countercurrent phase exchange takes place, the concept of the theoretical plate can be applied. Instead of the vapor-liquid equilibria, gas-adsorbate equilibria have to be used, which are expressed by the equilibrium curve, or in mathematical form by the separation factor. (Eq. 1).*

The following differences exist:

1. In the process and in the calculation of continuous gas chromatography, the adsorbent rate plays a very important role. (In the calculation method described in the literature (*5*)—applied only for Scheme 1—the importance of adsorbent rate is neglected, and a complete distillation analogy is used.)

2. There is no constant molal overflow, not even in the assumed case of isothermal conditions, because the quantity of the adsorbed phase varies according to its composition, which can be expressed by the formula of Lewis et al. (*6*), or by Eq. 3, which is a more suitable form for the further calculation.

The calculation itself involves the expressions of the material balances and equilibria, the determination of the height of this section (the number of theoretical plates), the location of feed point, and the reflux ratio.

The reflux ratio is defined—in the bottom section as well as in the upper section—as the ratio of the gas refluxed to the gas produced. This ratio is closely related to the adsorbent rate, as it is shown in Eq. 4. The adsorbent is always saturated with the adsorbed phase and, therefore, the quantity of gas desorbed per unit time is proportional to the adsorbent rate.

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* All equations are summarized in the appendix.

The total and the partial material balances of the column, as well as the balances of each theoretical plate can be expressed (Eqs. 5–7) according to Fig. 3.

The latter equations can be arranged in the form of Eqs. 8 and 9, which are the mathematical expressions of the operating lines, and which in the form of Eqs. 10 and 11, are suitable for plate-to-plate calculation, similar to those used in distillation.

This calculation can be accomplished in the following ways:

1. According to the *non-isothermal* nature of the process, but assuming adiabatic conditions, with the help of the heat balances around the individual plates, the volume can be calculated by a *trial and error* method. This method is long and complicated, and not even realistic, because of the heat losses on the walls.

2. Assuming an *isothermal* case, i.e., using a suitable average temperature, it is possible to express $W_{\min}$ and $n_{\min}$ in a *mathematical* formula (Eqs. 12 and 13). The calculation of the number of plates is carried out also plate-to-plate, but not by trial and error.

3. Neglecting the variation of the quantity of adsorbed phase and using an *average* one ($N = (N_a^\circ + N_b^\circ)/2$), the number of plates can be calculated *graphically* by the well-known McCabe Thiele method, which is not applicable in the isothermal case, because there the operating lines are not linear.

In all these cases the actual height of the rectification section is the product of the number of plates and the height equivalent to a theoretical plate (HETP).

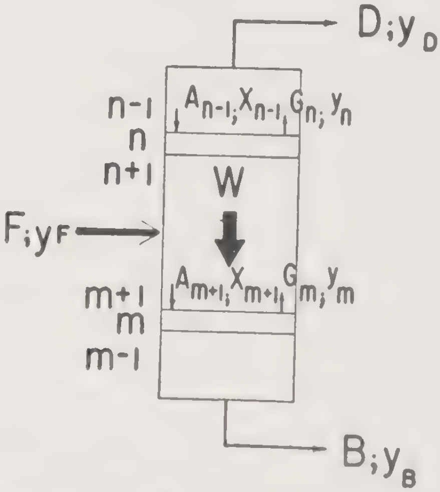


FIG. 3. Scheme 1. Material balance.

In the case of distillation, after the calculation of the minimum reflux ratio and number of plates, the actual values are then determined by an economic analysis. This is similar in continuous gas chromatography, but here—a very important difference—the adsorbent rate has to be very close to the minimum one, for the following reasons.

In distillation, and also in the continuous gas chromatography, the higher the reflux ratio, the lower the necessary number of plates, i.e., the height of the unit. In continuous gas chromatography, the reflux ratio is tied to the adsorbent rate. As this rate is increased, the necessary number of plates, i.e., the height of the rectification section, decreases. However, increased adsorbent rate is not desirable, because:

1. This increases the cost of circulation and increases the attrition loss, which are important expenses of the process.

2. The increase of the adsorbent rate decreases the residence time in the cooler and desorber, and the necessary height of these heat exchanger sections increases linearly (*7*) all other conditions remaining constant. Therefore, the height saved in the rectification section is lost twice, in the cost of the larger cooler and desorber.

In the calculation of Scheme 2 the following differences are to be considered:

1. This model has a separate frontal chromatographic section, which has to be calculated (*2*) for the total adsorption of the two components.

2. The gas mixture to be separated is introduced into the rectification section in an adsorbed phase. The result of this is that in the formulas for $W_{\min}$ the composition of the feed gas (calculated on an inert-free basis) is equal to the adsorbed phase and not to the gas phase, as in Scheme 1.

The final result of these facts is that the adsorbent rate is determined not only by the operation of the rectification section, but mainly by the chromatographic section, because of the lower partial pressure and, therefore, lower equilibrium adsorption values of the components to be recovered. The chromatographic section needs more adsorbent, and, therefore, the diameter of this section is greater than that of the upper part of the rectification section.

Scheme 3 is similar in construction to Scheme 1. The important difference is that the partial pressures of the adsorbable components are not the same above and below the feed introduction, which separates this section into frontal chromatographic and rectification zones.

The calculation of this chromatographic section is not as simple as in Scheme 2, because not only the feed gas, but also a reflux gas is introduced. It has to be designed to adsorb all the gas that is recovered, for instance, all the acetylene in the case of the separation of the partial oxidation gases of methane. The higher the acetylene content of the gases introduced in this section, the higher the quantity of activated carbon required for the complete adsorption of acetylene. It is desirable, therefore—from the standpoint of the adsorbent quantity— to introduce in this section the smallest possible quantity of this gas, i.e., the reflux gas has to have a low acetylene concentration. This low concentration can be obtained with a high rectification section and a high reflux ratio, i.e., with high adsorbent rate.

Consequently, there are two opposite tendencies of the adsorbent rate in the two parts: in the upper part the higher the acetylene content, the higher the required adsorbent rate; but the higher the adsorbent rate, the lower the concentration of acetylene in the reflux gas. The optimum velocity has to be calculated with regard to these two tendencies, and—with a method not detailed here—to determine and plot the various corresponding compositions and rates in both sections. The point of intersection of the two opposite curves gives the minimum value of adsorbent rate for this case.

This procedure involves the following steps (detailed in reference *4*).

(*a*) The $W_{\min}$ vs. y_1 relationship in the rectification section can be determined according to the point of intersection of the equilibrium curve and of the different operating lines (representing various adsorbent rates).

(*b*) The $W_{c\ \min}$ vs. y_1 relationship.

On the basis of the material balance the equation for the mole fraction of the less adsorbable component in the adsorbed phase (X_0) can be expressed at the point of the entry on the rectification section. The equation for the equilibrium gas phase composition (y_0) can be expressed by the material balance of the feed plate. These two phases are in equilibrium according to the equilibrium curve. After arranging these resulting three equations for the quantity of gas flowing up from the rectification section (G_1), a second order equation results and can be solved with various given y_1 values, where y_1 represents the mole fraction of the less adsorbable component in this gas.

(*c*) Using G_1, the combined partial pressure ($P_a + P_b$) of the two adsorbable components can be calculated, and from ($P_a + P_b$)—using the adsorption isotherms of the two components—the quantity of adsorbed phase per unit weight of adsorbent (N) can be determined.

(*d*) Knowing the different N values, the related W_c values can be calculated and the $W_{c\ \min}$ vs. y_1 relationship can be plotted.

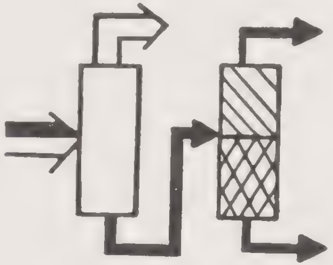
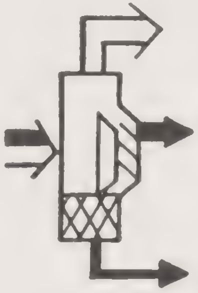
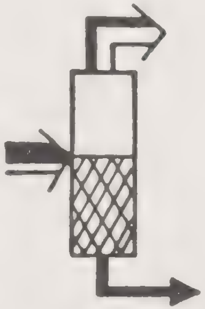
After the determination of the adsorbent rate, the further calculation of the column is similar to Scheme 1.

In Table I, the results of calculations obtained by these methods are presented for the three schemes, in the case of the separation of an acetylene, carbon dioxide, hydrogen mixture, at one atm. pressure, on Nuxit AL activated carbon. Case 1 represents a scheme where the acetylene and carbon dioxide are adsorbed in a separate chromatographic unit, and the binary mixture is separated according to Scheme 1. Cases 2 and 3 represent Schemes 2 and 3. The quantities of acetylene and carbon dioxide, and the permitted loss and impurities of acetylene are the same in all cases. A constant temperature is assumed (50°C), but the variation of the quantity of the adsorbed phase is not neglected. The actual carbon rates were calculated as 50% higher than the minimum ones, in those sections where the adsorbent rate can be determined from the rectification standpoint only.

Acknowledgement

The authors express their acknowledgement to the management of the Sinclair Research Laboratories, Inc. for making it possible to present this paper at the Symposium.

TABLE 1

Case No.	 1	 2	 3
Acetylene feed (mole/hr)	10	10	10
Carbon dioxide feed (mole/hr)	10	10	10
Hydrogen feed (mole/hr)	80	80	80
Acetylene loss permitted (mole %)	2	2	2
Impurities in acetylene permitted, (mole %)	2	2	2
W_v min (kg/hr)	(10.06)	(5.76)	—
W_l min (kg/hr)	(10.06)	(16.09)	—
$W_{\text{rect, actual}}$ (kg/hr)	15.09	8.64	25.74
W_c (kg/hr)	36.4	36.4	—
W total (kg/hr) = $W_c + W_{\text{rect, actual}}$	51.49	45.04	25.74
Number of plates in rectification sect	16	12.5	9

APPENDIX

The separation factor, α, is defined in terms similar to those in distillation:

$$\alpha = \frac{x_b y_a}{x_a y_b}$$

which for a simple binary reduces to

$$\alpha = \frac{(1 - x_a)y_a}{x_a(1 - y_a)}.$$

This shows the relationship for the composition of the two phases where α is constant. In other cases, the equilibrium curve itself must be used. For the relationship of the quantities adsorbed, the empirical relationship of Lewis (*6*) is used.

$$\frac{N_a}{N_a^\circ} + \frac{N_b}{N_b^\circ} = 1 \tag{1}$$

For a binary mixture, where

$$N = N_a + N_b \tag{2}$$

and

$$X_a = \frac{N_a}{N_a + N_b}$$

a new constant, β, may be defined

$$\beta = N_b^\circ / N_a^\circ$$

and through these relationships it can be shown that

$$N = \frac{N_b^\circ}{1 + (\beta - 1)x} \tag{3}$$

which is useful in deriving the equations for the operating lines. (In Eq. 3 and in the following equations x and y without subscripts refer to the lighter component.)

The reflux ratio is defined, similarly to simple distillation, as the ratio of the reflux stream to the product. However, in this case the adsorbent rate enters the expression, because the quantity of desorbed phase is proportional to the adsorbent rate. The reflux ratio for the lower section, for instance, is

$$R_l = \frac{WN - B}{B}. \tag{4}$$

The operating line equations are written as the usual material balances around plate "n" in the upper section and plate "m" in the lower section.

The overall balance for the lighter component (see Fig. 3) is:

$$Fy_F = Dy_D + By_B\,. \tag{5}$$

The balance around plate "n" in the upper section is:

$$G_n\, y_n = WN_{n-1}\, x_{n-1} + Dx_D \tag{6}$$

and around plate "m" in the lower section is:

$$G_m\, y_m = WN_{m+1}\, x_{m+1} - Bx_B\,. \tag{7}$$

(Eqs. 6 and 7 can be written in these forms, because on the bottom plate $x_B = y_B$ and on the top plate $x_D = y_D$.)

Whence the operating line for the upper section:

$$y_n = \frac{WN_{n-1}x_{n-1}}{WN_{n-1} + D} + \frac{Dx_D}{WN_{n-1} + D} \tag{8}$$

and the lower section:

$$y_m = \frac{WN_{m+1}x_{m+1}}{WN_{m+1} - B} - \frac{Bx_B}{WN_{m+1} - B}\,. \tag{9}$$

The operating lines can be expressed in a more convenient form for calculation by the use of Eq. 3 and the substitution of constants R_u° and R_1° defined as:

$$R_u^\circ = WN_b^\circ/D$$

$$R_l^\circ = WN_b^\circ/B$$

so that the upper operating line becomes:

$$y_n = \frac{[R_u^\circ + (\beta - 1)x_D]x_{n-1} + x_D}{(R_u^\circ + 1) + (\beta - 1)x_{n-1}} \tag{10}$$

and the lower operating line becomes:

$$y_m = \frac{[R_l^\circ - (\beta - 1)x_B]x_{m+1} - x_B}{(R_l^\circ - 1) - (\beta - 1)x_{m+1}}\,. \tag{11}$$

The equations for the minimum adsorbent rates are derived as follows.

Substituting in Eq. 10, the condition of the feed composition x_F and y_F

(at the minimum reflux ratio the operating line intersects the equilibrium curve at the feed composition), for the upper section:

$$y_F = \frac{[R_u{}^\circ_{\min} + (\beta - 1)x_D]x_F + x_D}{(R_u{}^\circ_{\min} + 1) + (\beta - 1)x_F}$$

$$R_u{}^\circ_{\min}(y_F - x_F) = x_D - y_F + (\beta - 1)x_F(x_D - y_F)$$

$$R_u{}^\circ_{\min} = \frac{W_{u\ \min}N_b{}^\circ}{D}$$

$$W_{u\ \min} = \frac{x_D - y_F}{y_F - x_F}\frac{D}{N_b{}^\circ}[1 + (\beta - 1)x_F]. \tag{12}$$

By similar reasoning, for the lower section:

$$W_{l\ \min} = \frac{y_F - x_B}{y_F - x_F}\frac{B}{N_b{}^\circ}[1 + (\beta - 1)x_F]. \tag{13}$$

GLOSSARY

A = adsorbed phase rate, mole/hr; $A = WN$
B = bottoms rate, mole/hr.
D = overhead rate, mole/hr.
F = feed rate, mole/hr.
G = internal gas phase rate, mole/hr.
N = adsorbed quantity, mole/kg adsorbent
R = reflux ratio
W = adsorbent rate, kg/hr.
x = mole fraction in adsorbed phase
y = mole fraction in gas phase
α = separation factor
β = constant

Superscript ° designates the pure component at mixture conditions, temperature, and pressure.

Subscripts: Upper case subscripts retain definitions above.

a, b	component designation
c	the chromatographic section
n	reference plate or fractionating zone above feed
m	reference plate or fractionating zone below feed
u	total zone above feed
l	total zone below feed

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Chapter XXIV

Past, Present, and Future of Gas Chromatography

A. J. P. Martin

An address before the ISA International Symposium on Gas Chromatography

Introduction

About sixteen years ago, in a paper relating to liquid-liquid partition chromatography which was published in the Biochemical Journal, there appeared the following comment: "The mobile phase need not be a liquid, but may be a vapor. Very refined separations of volatile substances should be possible in a column in which a permanent gas is made to flow over gel impregnated with a nonvolatile solvent, in which substances to be separated approximately obey Raoults Law. When differences of volatility are too small to permit a ready separation by these means, advantage may be taken in some cases of deviation from the Raoults Law as in azeotropic distillation".

With these words, Drs. Martin and Synge stated, in effect, all that has been achieved in gas chromatography. Dr. Martin has been with us this week as our honored guest, helping us to explore the far-reaching possibilities of this interesting concept.

Dr. A. J. P. Martin was born in 1910 and was educated at Bedford School and Peterhouse, Cambridge, England. He held a Grocers Research Scholarship at the Nutritional Laboratory at Cambridge and then joined the Wool Industry Research Association as a Biochemist in 1938. Here, he worked with R. L. M. Synge. Together, they discovered the technique of liquid-liquid partition chromatography. He later held a post at Boots Pure Drug Limited before moving to the National Institute for Medical Research at Mill Hill, London, where, with A. T. James, he developed gas-liquid chromatography. He now works with his own organization at Abbotsbury, Elstree, Herts. Dr. Martin was elected a fellow of the Royal Society in 1950. He was awarded the Berzelius Gold Medal of the Swedish Medical Society in 1951, and in 1952 he and Synge won the Nobel Prize in chemistry in recognition of their discovery of liquid-liquid partition chromatography.

Without further comment, it is my great honor to present Dr. Martin, who will talk with us about gas chromatography—past, present, and future.

ADDRESS

Mr. Wherry, Vincent Coates, and Henry Noebels, and the Instrument Society of America, I thank you very much for this opportunity to attend this most stimulating meeting. The title which I was given for this lecture, "Past, Present, and Future of Gas Chromatography", is one which I was very happy to accept.

Beginning with the past, it affords me an opportunity of saying—which everyone has learned I enjoy saying very much—that I thought of it all a long time ago. My interest in chromatography began in about 1932 with the running of what I believe was the first chromatogram that was made in England. I was, at that time, interested mostly in attempting to purify Vitamin E. In addition to using solid-liquid chromatography of the classical Tswett-type in this work, I also started to investigate counter-current extraction with two liquids. This required the building of a somewhat elaborate machine (around 1935) which had an efficiency of some 200 theoretical plates. (I would have you to note that this theoretical plate concept came to me as a biochemist rather than as an oil engineer, and it started before I was able to apply it to chromatography.*) This machine of mine took a lot of watching. It was a delightful machine with some 300 feet of glass tubing in it. As it ran, it made a noise like waves coming in on the beach, due to the 90 ball valves in it that rattled on their seats every few seconds. You had to sit by this machine in constant attendance in case bubbles occurred in its entrails, which frequently happened, or emulsions became too troublesome. But it did do a job. It separated Vitamin E, showing more than one form of Vitamin E in the days before Vitamin E had actually been isolated.

Later on, while I was still at Cambridge, Synge was working in the Biochemical Laboratory trying to separate amino acids using the big differences in the partition coefficients of acetyl amino acids between chloroform and water. He came to me to see whether my machine would help him in his work. We very soon found that it wouldn't, so we built another machine. Eventually, I moved to the Wool Industries Association at Leeds and succeeded in getting Synge to join me there to continue his work. Soon, we had another fantastic machine—this one a menace to health as well as being a pretty thing to watch. It filled the room with chloroform. This machine also required constant attendance; we used to take turns, each would sit by it for eight hours at a time. Among other things, we discovered the peculiar effects of chloroform intoxication. It has a deplorable effect on one's temper. Whenever the other one appeared after a session of this, he was always greeted with violent abuse. Another curious effect was that fresh air had a characteristic, yet remarkably peculiar smell. Well, I designed a new type of counter-current machine about once a week until Synge got fairly tired of hearing about them. Actually, they were all too difficult to make.

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* Dr. Martin is referring to a rather lively debate held earlier in the day of HETP versus performance factors.

One day, it suddenly occurred to me that the difficulty we were encountering in designing a good machine was that in order to get rapid equilibrium between the two phases we had to make the droplets very small indeed. But, as soon as we made the droplets very small it was virtually impossible to make them move in the direction you wanted them to move. So, it occurred to me on this occasion that I was beating my head quite unnecessarily against the wall; all we had to do was to hold the droplets still and make the liquid flow through them. So, we took some silica gel and we ground it up, sieved it, put some water on it, and put some acetyl amino acids on the top and ran them down with chloroform. By the next day, we had demonstrated that we could separate acetyl leucine and acetyl alanine by this technique. A day or two later, we incorporated an indicator in the system and could watch these bands move down; from this we had the first partition chromatogram. We then, naturally, started to generalize and realized that not only could we use a great many different things to hold the water, but we could use a great many different liquid systems. We had a very powerful tool at our disposal. We had very many headaches working this system out—the reasons I have no time to go into.

Eventually, the method was made to work nicely, and when we came to write up the paper for the Biochemical Journal, the speculations noted in the paragraph mentioned previously were included. We had no doubt that this was a useable method but neither of us was interested in volatile substances at that time. Our interest in proteins and peptides, particularly with respect to the elucidation of the simple peptides, kept us very busy with paper and partition chromatography over the next few years. Eventually, I joined the National Institute for Medical Research in Mill Hill. There I had as an assistant, Dr. A. T. James. He and I began to attempt to put crystallization on a column basis. We had various, somewhat complicated arrangements and we worked at it for a couple of months and we could still do an awful lot better with two beakers than we could with all the apparatus we had made. We found this rather discouraging. I was very used to discouragement by this time, but Dr. James was not quite so used to it and rather felt that our approach was a complete waste of time. I agreed and suggested that we try something that I was quite sure would work. I suggested that we use what is now called gas chromatography. I didn't, at that time, foresee quite how far it would spread, but within a few weeks we had a working gas chromatograph separating fatty acids and the simpler amines. This kept us busy for a couple of years. During this time, we had a visit from Dr. Ray. He was one of the first people who wanted to use the method for other problems. Several others, however, had indicated they wanted to use exactly our technique to duplicate the work on the same fatty acid problems that we had already worked out.

Dr. Ray, however, wanted to examine compounds which were not detectable by titration. We sent him away with two suggestions, as I remember; one that he should use the katharometer which Claesson had already used as a detector for his gas-solid chromatograms and, two, that he should hitch up to it an infrared spectrometer with a cathode ray oscilloscope so that he could watch the bands change as the components came through. Much to my regret, I don't think he ever did the latter. I am not aware that anyone else has done this either. I would like to see this done. It would make a very pretty picture.

Now from that time, gas chromatography began to get out of hand. I had a delightful couple of years when I could tell people what I was doing without anybody telling me anything. This was a situation which I enjoyed very much. I had the same experience with paper chromatography when people would come, observe, and be suitably impressed. Nobody had done enough work to argue. Now, of course, this is very far from being true. The pleasant, easy life has gone long since. At the present time, I have no idea how many people are working on gas chromatography throughout the world, but to borrow a bacteriologist's phrase, it still seems to be in the logarithmic phase.

Now speaking about the Past, I must mention my friends of the Shell Amsterdam Laboratory who have done so much of the initial theoretical and practical work on gas chromatography. It was only a very short time before I went over to Shell Amsterdam to find that there were some dozens of people more or less concerned with gas chromatography over there, and I began to feel that I was thoroughly understaffed with two or three people working on the method.

As for the Present, I don't really need to tell you very much about the present position of gas chromatography. Its general characteristic seems to be the rapid application of well-known methods to an infinity of problems. This is what most of you are engaged upon, and it's obviously going to be a phase which lasts for a very long time. There are so many problems which can quite obviously be tackled by these means that this phase of growth is going to continue for some considerable time to come.

Now, as to the Future, I gather I have gained some reputation as a prophet in these matters, and prophecy is certainly what is called for here. When you feel that you are a leader in a field, you can fairly safely prophesy what you want to happen, even if you can't prophesy what is going to happen. You have a fairly clear idea of a number of leads which you think it profitable to follow up, but by the time some thousands of people have ideas on the subject, prophecy seems to become a rather unprofitable occupation.

One of the things which has come from this meeting which I've been delighted to see is that this is regarded as an educational and moral subject. I have heard it said that we, the users of gas chromatography, are educating the organic chemists and physical chemists and instilling moral principles into suppliers of chemicals, as well as the people who write papers. Insisting more or less by our mere presence that people know what they are selling and what they are claiming to be pure substances. It is delightful to be a moral force in this way. I've never felt it before. I was particularly struck by the phrase of one contributor that "people were honest by chromatography." I'd like to point out one other kind of way in which I feel the chromatographer is a benefactor of the human race. He makes two peaks grow where only one grew before. Now, the one thing which I definitely was prophecying a few years ago I think has now come to pass, and that was that analytical distillation is obsolete. I think there are remarkably few cases now where distillation is used as an analytical tool which could not better be done by gas chromatography. This is not an absolute rule, but I think that it is pretty safe to say this.

If we consider various items about chromatography and what advances could be expected in them—I suggested in one of my papers not very long back, that there would not be any very serious improvements in the solid support for the stationary phase. I had reason, on thinking this statement over, to doubt my own words almost immediately. I started thinking about empty tubes. Dr. Marcel Golay has also been thinking about empty tubes, obviously before I was thinking about them. He has now shown that nothing is an excellent packing. So, I would like to thank him for nothing. This paper, I must say, is the highlight of the meeting as far as I'm concerned here. It was my principal reason for wanting to come to see whether my worst fears were confirmed, as indeed they were. I'm quite sure that this is a method which many of us are going to pursue with considerable enthusiasm from now on. It's too early yet to say how useful it's going to be, but it is quite clearly something that we should all know about.

Obviously, people are going to move to higher and higher temperatures. No one is ever content with what a good method will do. There are always attempts to push it to what it won't do. So, we are all going to be asked to run non-volatile substances. The only way we can attempt to do it, as far as I can see at the moment, is to run the columns hotter and hotter. Eventually, thermal decomposition will overcome us and the components will break up before they get to the other end of the column. Not only have we to contend with the substances themselves breaking up, but with the stationary phase decomposing as well. I don't think I have anything to contribute on this. Many experienced people are following this investigational course, and we can certainly expect, in the relatively near future, a large number of suggested substances for high temperature stationary phases.

One of the things which was mentioned here by Courtenay Phillips is metal salts. These are interesting in very many respects, particularly in that here we may have something with a very high degree of specificity.

In this field of finding stationary phases of high specificity, lies work for very many years to come. This appears to me to be an extremely difficult field; as difficult as it is obviously rewarding. Many of you may know of Dickey's work done at the California Institute of Technology. He took silica gel and found that if he made this gel in the presence of methyl or ethyl orange, that under certain very specific conditions it had an ability to adsorb more of the particular substance in whose presence the gel was formed. He had tailor-made an adsorbent to fit the molecule. This work has been astonishingly neglected. Few people have done work on it since, but here, clearly, is a lead. How if should be followed, I can't tell, but here is a lead indicating that it is possible, in certain cases, to make an adsorbent which will fit a particular molecule. If we can do this on the solid phases which can be used for gas chromatography, we may be able to solve those otherwise almost unsolvable problems requiring a particular substance to be picked out of a nasty mess.

I might say here that this—having to deal with the nasty mess—is perhaps the most fruitful thing that can happen to any analytical chemist. I remarked earlier this evening that I felt that biochemists had been responsible for far more than their share of new developments in analytical chemistry, and this is surely because they are faced with intractable mixtures about which they know practically nothing. All they know is that there is something there they want to get out and if you can't get it out by any means at present known, you are driven to think of a new means.

Now, another very active field at the moment is, of course, detectors. We've heard a lot about katharometers of one kind or another at this meeting and I will venture a rash statement that they are already becoming obsolete. I know they will be used for a long time to come and they will always be used for certain purposes; but there appears to me, at the moment, to be an entirely undue amount of concentration upon katharometers. There are many other methods which have been suggested. Phillips has suggested half a dozen, and I have suggested half a dozen, and many other people have suggested workable methods of different kinds. Of the present methods, those involving ionization of the gas in one way or another have obviously come to stay. In what form, I can't tell, but I'm sure that a method involving ionization will be one of the principal methods which will be evolved. Here you have something which can be made to occur in the molecules which you are trying to separate and not in the carrier gas. Here you have the possibility of a sensitivity of quite a different order from what you can expect in the change of any general property of the gas as a whole.

If you have to deal with a method which involves all the molecules in the system in one way or another, it cannot possibly be ultimately as sensitive as one which can pick out the individual molecules that you are interested in. Any satisfactory extremely sensitive method must be one which is not affected by, nor depends upon, the carrier gas, but, depends upon only the substances that you are interested in, as well as the traces of the supposedly stationary liquid phase that contaminates the gas due to its partial pressure.

Now, on the subject of long columns and difficult resolutions, there was a suggestion yesterday that one separation would require a column a quarter of a mile long. This was thought to be excessive. I would like to suggest that there is nothing excessive about a column a quarter of a mile long. There may be many jobs which you can do only on columns a quarter of a mile long, and if that's true, some people will do them. At the moment, I don't think we need go to these lengths because there is another suggestion which I made quite a long time ago that will enable us to run the substances a quarter of a mile very easily without requiring a column a fraction of that length. If you have two columns and you have two substances that are very difficult to separate, you can arrange to drive the pair of substances into the first column and then when it gets near one end you connect it to the other column and you continue blowing until it's gone right into the second column, monitoring its passage with an extremely small detector, probably a katharometer in this case. When it is safely in the second column, you disconnect the first column and start blowing in the end of the second column, and carry on until it's started into the first one again. And so you go on, round and round and round, until the bands have become too wide to stay within the column. Now, this I suggested a long time ago to a lot of people, but nobody seems to have taken any interest in it. You can easily calculate that you can get efficiencies from these columns which should enable one to separate, say a ^{13}C from a ^{12}C compound. This, with methanol or with chloroform, I'm sure would be reasonably easy. Perhaps if you take a larger molecule it will be a bit more tricky. These things can be separated very usefully by distillation at the moment. And, if we can't do a better job than the distillation boys, we ought to be ashamed of ourselves.

On the subject of the number of theoretical plates and comparing the number of theoretical plates in a chromatogram and in a distillation column—I think a lot of people concerned with distillation are very irritated by this because they say, "We have a distillation column with 200 plates and it will do a better job than your column of 3000 plates. Therefore, what do you mean by using the same word for it." This is not a reasonable attitude to take, in my opinion, because what you should compare is the length of column occupied by the zones in question. This, then, is reasonably comparable with the distillation column. If your zones occupy 200 plates, then you are getting separations corresponding to what a 200 plate column does and, of course, you're getting it a great deal quicker. But, in order to make your zones occupy 200 plates, you have had to run it down some thousandths of plates down the length of the column. If you use the recirculation idea, you will probably find that you can work with columns where you can get complete separations such as you can get with distillation with columns which have 5 or 6 times as many plates as those involving the distillation column itself. I don't think I have time to go into just what these relations are, but they are very simple and I did give them at a meeting last year in Lisbon at the International Congress of Pure and Applied Chemistry.

The use of gas chromatography for preparative purposes is an application we have heard a little about today. There is no doubt whatever that for the preparation of highly pure samples, gas chromatography offers one of the best and most convenient methods, if you are not after too great a quantity. I believe even if a couple of kilograms of very high purity material are needed, it still is easier and quicker to obtain this by gas chromatography rather than distillation. People who are particularly interested in pure hydrocarbons are in the habit of running their distillation columns continuously for six months at a time. You can run a few grams fairly quickly compared to this, even though it is a very difficult separation, and you should be able to run it enough times to build up quantity. So, I think for small quantities of materials, gas chromatography is strictly competitive with distillation. For very difficult separations indeed, there is no question as to its profitability. On a very large scale, gas chromatography, as such, doesn't seem likely to be a useable separation method. The cost of pumping the enormous volumes of dilute gas around the system will always be greater than working at the comparatively greater concentrations which you can do with distillation. Possibly the only exception to this would be in the case where very high purity is required. An example of this, I believe, is in the preparation of extremely pure silicon for electronic purposes, which contains less than one part of impurity in 10^{16} parts of silicon.

There are specialized problems to which gas chromatography is particularly applicable. Problems involving flavor, odor, and the isolation of other substances of biological interest have one thing in common. You have to isolate extremely small quantities of active material from enormous quantities of inert unwanted matter. I have observed, in speaking to people in this field, that many workers are obsessed by the idea of achieving this isolation in one operation. I think we must think carefully about this. In all probability, one will have to employ a kind of cascade system with large columns to make the initial separation, and then gradually narrow the sample down by using smaller, more efficient, and different types of columns at later stages.

Detectors of biological origin—there are obviously fascinating possibilities here. Insects which detect things, such as cockroaches, gypsy moths, etc., could obviously be placed at the end of the column, and by watching their activities, one could conceivably determine what was coming out. There is really nothing fantastic about this idea, it ought to work. Another one which perhaps is not quite so easily done is to employ something with a good nose—a dog—to detect the substances coming out. This again is something you can probably do. You could train animals to detect different substances. I think that the dog can smell a detailed picture in much the same manner as we perceive detail through vision. If you could just find out how to talk to him, he undoubtedly could tell you a great deal.

There are various other uses of gas chromatograms, such as in the collection of thermodynamic data. It can be used for various odd jobs, like the study of catalysts. You can mount a catalyst almost immediately above your column and you can put a sample through the catalyst while operating under specific conditions. As it comes through, in perhaps a few minutes, you can get complete information about this. Immediately then, you could alter your experimental conditions and repeat the runs. Probably, this would enable one to do ten times as many experiments a day as have been done by the previous methods; this, of course, won't give you ten times as much information, perhaps, but you still ought to get on a lot quicker.

A most entertaining suggestion comes from the Shell Laboratory of Amsterdam. Dr. Keulemans mentioned to me a long time ago that you can use gas chromatography to give you a lot of information about substances which cannot be run directly on the gas chromatogram by simply cracking them before they go in. If you have a hot bed on the top of the column that is suitable for cracking conditions, then you can get extremely reproducible patterns for a whole lot of substances which could not be run on the chromatogram by themselves. This, after all, will give you information very much like that obtained with the mass spectrograph. You do, in the mass spectrograph, in fact, examine a cracking pattern. There is no reason why we shouldn't do the same thing on the gas chromatogram. I feel, myself, this has a great future; particularly for people who are investigating structures of unknown substances. I think it would eliminate an enormous amount of the work which is presently involved.

Now, the use of the gas chromatograms as an aid to automation needs no laboring from me. It is obvious to everybody that if you put in a little bit of gadgetry, you can make the gas chromatogram run without the attention of the chemist. If you take samples at intervals, it will turn out results at short intervals, perhaps, with our empty columns, even a few seconds after we put them in. In this case, we become directly competitive in speed with the mass spectrograph. Such chromatographs can obviously, again with gadgetry of perfectly understood character, be tied into automatic control of apparatus of any kind.

There is the question of the presentation of the data from gas chromatograms. At the moment, people are content to get miles of paper which literally trial over the floors and pile up on the benches and are covered mostly with red lines. Unfortunately, these things have to be looked at, usually, and this employs a lot of people in a very dull way, measuring peaks. This is a job which we ought not, at the present time, inflict on people. Of course, this all means more apparatus, more instrumentation. It was a great grief to me when I moved from paper chromatography to gas chromatography to find that I had to buy a recorder, or make one. I had a feeling that a good method just was something that you could pick out anywhere in the lab and start out without having to go somewhere to get approvals or a grant, or get this and get that. There is a very urgent need, at the present time, for people to make not only cheap gas chromatographs with glow plugs in them, which is a delightful idea, but we want the glow plug analog of the recorder.* I'm waiting for someone to produce this. I mean not something costing even one hundred dollars, but five dollars. In certain cases for people who do a lot of work, it is desirable to eliminate as much manual labor as possible. Of course, as an instrument society, it should be an axiom that any piece of apparatus is less expensive when purchased from the manufacturer than made by yourself. Since I have become a manufacturer (I must be the smallest manufacturer of gas chromatographic apparatus in the world, I have sold eight pieces so far) I fully agree with this point of view. There are a number of applications for a gadget that could be attached to a recorder to allow the direct presentation of an integrated value. Of course, there are various tricks and devices currently available to allow approximate integration, but most people working in this field would prefer to obtain the product of a true integration figure multiplied by the appropriate factor.

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* Dr. Martin is referring to a paper presented by Felton, of duPont, on a simple gas chromatograph using model airplane glow plugs as detectors.

If we tie the gas chromatograph to other pieces of laboratory equipment, we have the possibility of almost the automatic chemist. We can separate a substance on the gas chromatograph, we can take every column which is reasonable in turn, and substances as they run from the column can go directly to various instruments such as nuclear magnetic resonance, ultraviolet, visible, infrared spectroscopy, and we can have a mass spectrograph working as well. Here you have the uniting instrument of the gas chromatograph in the center with its slaves clustered around. The calculating machine in the background which will have the records of all previous substances separated on its magnetic drums, and it will come out with a sheet typed at the end with the name of the compound and the weight per cent in the mixture. We may even get it to the stage where it will work out the structure too. This may be some distance in the future, but I feel this is a good note on which to finish.

CHAPTER XXV

Chromatographic Analyzers in Process Instrumentation

B. O. AYERS

Phillips Petroleum Company, Research and Development Department, Process Development Division, Bartlesville, Oklahoma

INTRODUCTION

Recent technological advances and increased demand for products from the chemical and petrochemical industries have led to more expensive processing plants. For the greatest economic return, these plants must be operated at maximum efficiency both from the standpoint of throughput and utilization of raw materials. Suitable process instrumentation is an important factor in improving the efficiency of plant operations. As plants have increased in size and complexity, the extent of instrumentation of the plants has increased proportionately. There has also been a corresponding increase in the precision of measurement demanded from these instruments. For example, new and improved devices for flow rate measurement and control continue to appear although such measurements are basic to continuous chemical processing and were among the first process variables to be automatically measured and controlled. New techniques for the measurement of physical and chemical properties are examined and those which prove suitable for the purpose eventually find their way into process instrument use.

Current trends in process instrumentation are toward an increasing use of composition analyzers. Infrared and ultraviolet analyzers and process refractometers are now widely used for monitoring chemical composition and in automatic control service. The success achieved with these analyzers has led to closer scrutiny of laboratory analytical methods as the basis for developing process composition analyzers.

One of the most successful recent developments in laboratory techniques has been based on gas-liquid partition chromatography. A cursory survey of the literature for the past five years will show the enormous potential of gas chromatography for the analysis of process streams, particularly those in the petroleum and petrochemical industries.

In this case, thanks to experience gained with ultraviolet and infrared analyzers, the transition from laboratory instrumentation to practical process analyzers has occurred quickly and a number of process chromatographic analyzers have been placed on the market.

Process Chromatographic Analyzers

There are a number of performance standards and design specifications which are considered requisite to acceptable process analyzers. Among the most important of these are:

1. Operation must be automatic and stable for extended periods of time.
2. The analyzer must not introduce safety hazards into operating or control room areas.
3. The analyzer must be accepted by operating personnel as reliable and must make a real contribution to the operation of the processing unit.
4. Data must be presented in a readily intelligible and usable form.
5. Analytical results must meet minimum standards of accuracy and reproducibility.
6. Instrument response time must be compatible with time constants of associated processes.
7. The associated sampling system must provide a sample that is representative of the process stream without disturbing the process and without introducing appreciable time lag into analyzer response.

These demands are applicable to all process stream analyzers. The instrumentation required in each case depends on the physical or chemical property measured and the variation in the measured property with changes in operating parameters of the analyzer.

In the case of a chromatographic analyzer, the sequential nature of the analysis is a distinguishing feature and is an important factor in instrument design. A process chromatographic analyzer must automatically perform the following functions:

1. Measure a fixed quantity of sample.
2. Add sample to chromatographic column.
3. Elute sample components from column.
4. Detect and measure concentrations of sample components in column effluent.
5. Record analytical data in intelligible form.
6. Repeat these steps automatically and reproducibly.

Operation of an elution chromatographic column is illustrated in Fig. 1. When operating variables such as temperature, carrier gas flow rate, column efficiency, detector sensitivity, and sample size are maintained constant, the time at which a sample component emerges from the column is characteristic of the component and the peak height is proportional to the concentration. For a process analyzer, instrumentation must be provided to control these variables to the required constancy and a sequence timer or programmer must be added.

For clarity of discussion, the components of a process chromatographic analyzer can best be divided into the analyzer unit, sampling system, and programmer unit. A process chromatographic analyzer is shown in block diagram in Fig. 2.

The analyzer unit is designed to be located in the plant near the process

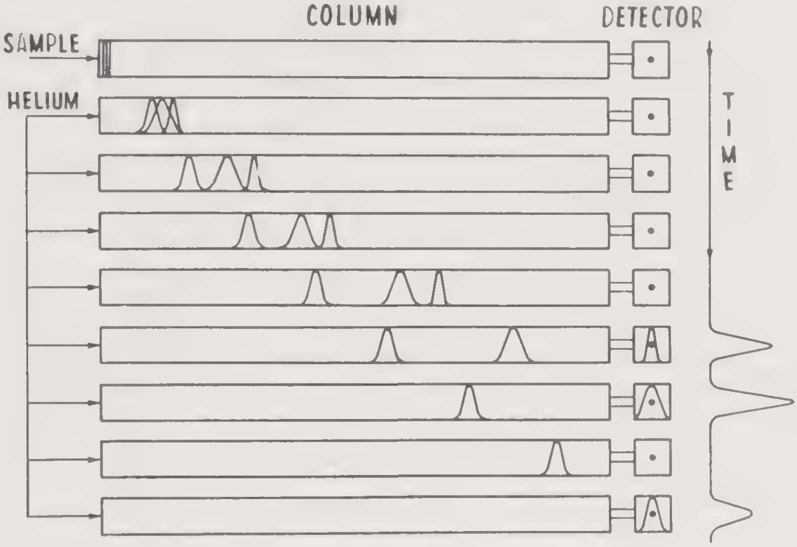

FIG. 1. Schematic of column operation.

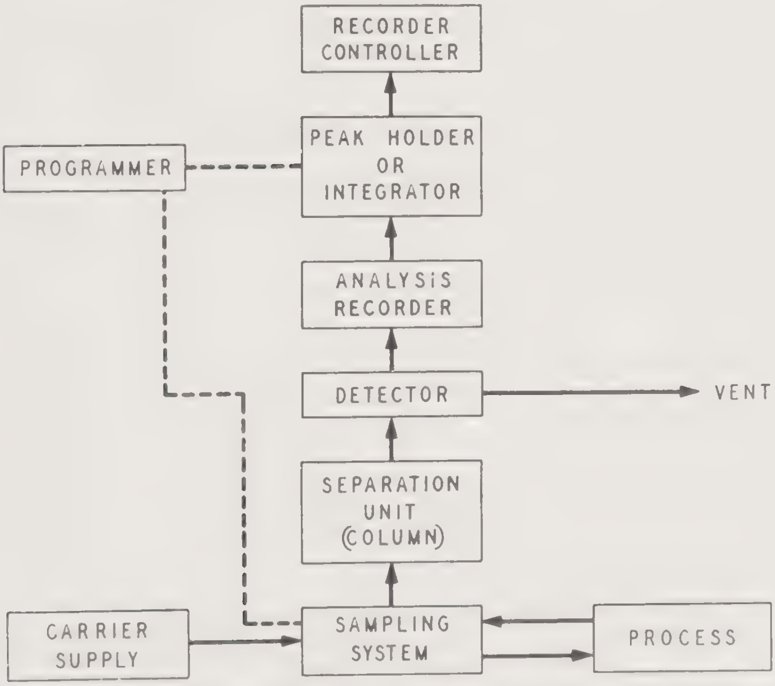

FIG. 2. Block diagram of process analyzer.

stream to be analyzed. The analyzer is enclosed in a housing suitable for installation in Class I, Group D Division I hazardous locations. The unit contains the chromatographic column, detector cell, sample valve, and carrier gas flow control system. Each of these is affected to varying degrees by fluctuations in temperature and must be housed in a constant temperature enclosure. The temperature of the enclosure is controlled to about ±0.2°C either by intermittent electrical heating or by a proportional controller which regulates the ratio of hot and cold air blown through the analyzer housing. The analyzer is usually designed to provide the required temperature control over an ambient temperature range of about −20 to 120°F. The column and detector must then be operated at a minimum of about 140°F to permit adequate thermostatic control at the highest ambient temperature.

Chromatographic column packings for use in process analyzers are in general the same as those used in the laboratory. However, in process analyzers the columns operate at higher temperatures and a few days of operation may be equivalent to years of operation in the laboratory.

Operation of chromatographic columns at elevated temperatures has two deteriorative effects. Many liquids which are highly useful at room temperature are unstable at the temperatures required for process analyzers. Distillation of these liquids from the chromatographic column results in continuously changing column characteristics, contamination of the detector, and a decrease in useful column life. A second effect of operating the column at higher temperatures is the decreased efficiency of chromatographic separations. This can be compensated for, in part, by increasing the column length. Additional compensation can be obtained in many cases by improving the resolution of the detector cell. Improved separations at higher temperatures may sometimes be obtained through the use of series column combinations (*5*). Success of this method depends on selection of two stable column materials which, in series, will make separations not accomplished by either column alone.

Another factor to be considered in the choice of column packing is irreversible reaction with a component of the sample stream. It is often possible to remove interfering components in the sample preparation system, but this may lead to the use of a complicated and expensive sampling system. In such cases it may be preferable to exercise greater care in the choice of the column packing to be used. Thus if two column materials will provide the required separations, that material should be chosen which is least likely to react irreversibly with any component of the sample. For example, water, a prevalent contaminant in process streams, is often difficult to remove without changing sample composition. Use of less polar column packing, where practical, will increase the water concentration that can be tolerated.

Interference caused by water and high boiling impurities can sometimes be removed by using two columns in series separated by an automatic valving arrangement. The packing for the first or splitter column is chosen to retain the interfering components while the components of interest move into the analyzer column. Impurities are flushed from the splitter column while a separate stream of carrier gas elutes sample components from the second column. An example of an arrangement of this type is the use of a silicone column to remove water from a sample of permanent gases and low molecular weight hydrocarbons.

After sample components have been separated by the chromatographic column, some means must be provided to measure their respective concentrations in the effluent gas from the column. As was the case for laboratory instrumentation, measurement of thermal conductivities has proved to be best suited for this purpose. Process instrumentation, however, demands a higher degree of long term detector stability.

Wire filament and thermistor bead detectors are used for process analyzers. Wire filaments provide better long term stability but with appreciably less sensitivity. Compensation for zero drift of the detector may be obtained by programming an automatic bridge zero adjustment into the analyzer cycle.

Both types of detectors are temperature sensitive and with some types of gas flow geometries are flow and pressure sensitive as well. The detectors must therefore be located in a constant temperature environment and carrier gas flow rate must be closely regulated.

Variations in carrier gas flow rates also affect the retention times of the sample components. Since the process analyzers operate on a timed-sequence basis the retention times and hence carrier gas flow rates must be reproduced within close tolerances.

Rate of flow of carrier gas in controlled by spring-loaded pressure regulators or differential pressure flow controllers. Both types of regulators are temperature sensitive and are affected by fluctuations in atmospheric pressure. Errors caused by temperature fluctuations are minimized by placing the regulators in a constant temperature enclosure. Pressure fluctuations arising from variations in atmospheric pressure can be removed by use of absolute pressure regulators.

Since a chromatographic analyzer operates on a cyclic basis, sample must be added to the column once per cycle. The sample quantity, approximately one ml of gas or vapor, must be reproduced accurately in order that chromatographic peak heights may be used for quantitative measurements. Sample addition must also be automatic.

An automatic gas sampling valve is shown schematically in Fig. 3. In position 1, carrier gas flows through the reference detector, sample loop, chromatographic column, sample detector, and to vent. During this interval, sample passes through the valve block to vent. In position 2, sample passes through the sample loop while carrier gas is bypassed to the column. After the sample loop has been purged, the valve again rotates to position 1, trapping a fixed quantity of sample in the sample loop. The sample is carried to the column by carrier gas and normal operation continues.

Clean sample, representative of the process stream, must be provided to the sample valve. Sampling systems may range from the use of simple components such as pressure regulators or vaporizer-regulators for clean noncorrosive samples to the use of elaborate sample preparation systems for the removal of entrained liquids and solids.

Figure 4 shows a sampling installation for clean liquid streams. The vaporizer-regulator is placed at the sampling point in order to conserve on sample quantity. The sample line is steam traced between the sample point and the analyzer. In order to reduce time lag in the sample line, it is necessary to bypass sample to a low pressure point in the process stream or to vent.

An example of a complex sample preparation system is illustrated in Fig. 5. This system was designed for the complete removal of entrained solids from the sample stream.

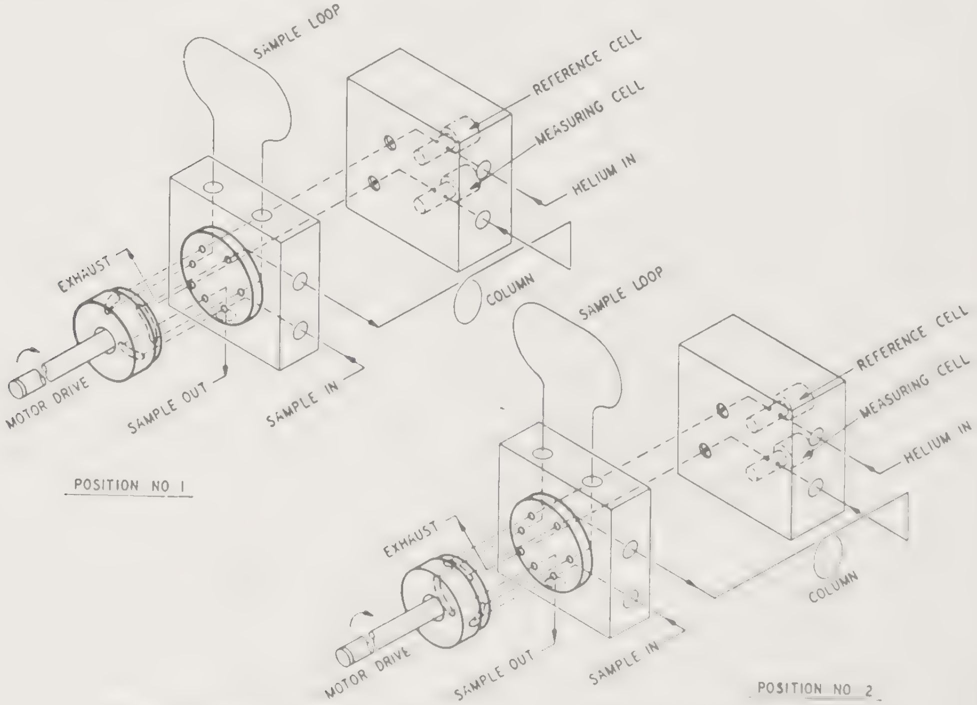

FIG. 3. Sample valve for process chromatographic analyzer.

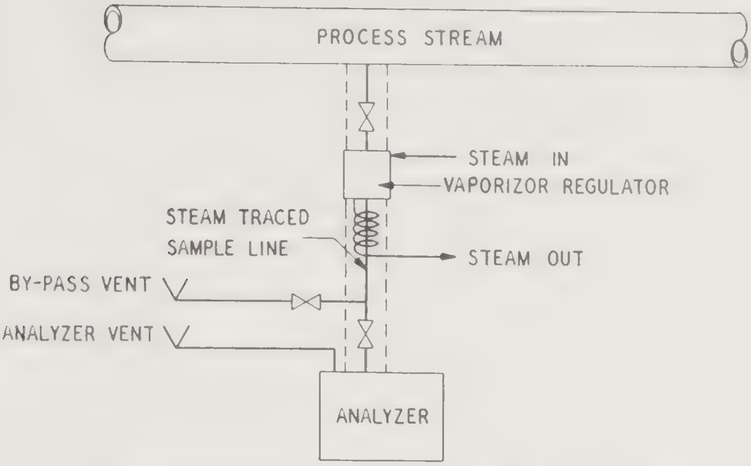

FIG. 4. Sampling system for clean liquid streams.

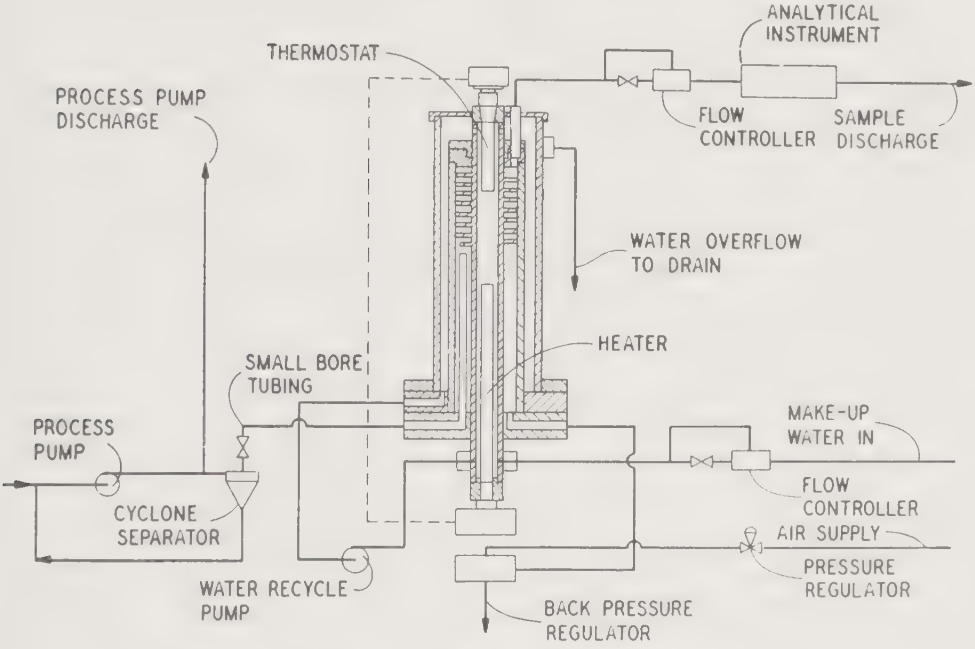

FIG. 5. Schematic of flash system for solids removal.

In this system, liquid sample is flashed under controlled temperature and pressure conditions. The flashed vapor supplies the sample to the analyzer. Liquid remaining after the flashing operation carries away the entrained solids.

Pressure control of the flash chamber is obtained by the use of a back pressure regulator specially designed to discharge heavy liquids and entrained solids from the chamber. Temperature control is accomplished by circulating water at constant temperature through the chamber jacket and through a heat exchanger in the chamber. Water temperature is controlled with an electrical heater and a thermostat. Cold make up water is continuously added to the circulating system.

These examples illustrate the extremes which may be encountered in sampling problems. In some applications, the sample preparation system is, in itself, a small processing unit. It is not surprising therefore to find that in some installations the cost of the sampling system is equal to, or greater than, the cost of the analyzer.

Data Display

Choice of the most suitable type of data presentation for process chromatographic analyzers is complicated by the wealth of data available and the cyclic nature of the analyses. The most straightforward method is recording of the complete chromatogram. This type of presentation is difficult to read and is wasteful of chart paper. Another disadvantage of chromatogram presentation is that the length of chart visible at any time is such that concentration trends are not obvious at a glance. Some compromise must be reached between the number of components to be recorded and the intelligibility of the record.

In many cases, the concentration of only one component is required for control purposes but additional information may be useful as an indication of process upsets or as a measure of product purity.

Common practice is to pick a maximum of four or five key components to be recorded and to reject the detector signal for other components by means of switches controlled by the programmer. The three methods in general use for recording these components are bar graph recording, peak recording, and multipoint recording.

Bar graph presentation is obtained by stopping the recorder chart drive while the sample component of interest passes through the detector. The chromatographic peak is compressed into a bar on the recorder chart. The chart is advanced a predetermined distance between peaks. The record consists of a series of bars along the recorder chart whose heights are proportional to the concentration of the sample components. Additional spacing or other reference marks identify the start of each analysis cycle.

If the recorder chart is stopped between peaks and allowed to move while the sample component passes through the detector, the record consists of a series of chromatographic peaks. Two advantages of peak presentation are that checks on the elution time of a component can be easily made and that the appearance of an unknown component can be readily detected.

A third and in many ways a more attractive method of data display consists of presenting analyzer readings as colored curves, one for each component of interest. Despite the advantages of this method with respect to clarity and condensed form of recorded data, it has been little used because of the additional expense of a recorder of this type.

In general, peak height is an adequate measure of concentration but there are instances where integrated peak areas may be preferred. If the chromatographic peak is broad and diffuse, peak height is relatively insensitive to changes in concentration and peak area gives better results. However, unless the range of components to be analyzed is extremely large, instrument parameters can be adjusted in most cases to give sharper peaks for which peak height measurements are adequate. There are, however, analytical problems where peak area measurements are extremely useful. Such, for example, would be the case if the total concentration of C_4 hydrocarbons is desired, since the summation of integrated peak areas is generally easier than the summation of peak heights.

Operation of a process chromatographic analyzer is controlled by a sequence timer or programmer. Two types of timer mechanisms are used: a timer motor-multicam arrangement and a timer disc. In either case, a cam or timer disc tab actuates the sampling valve to initiate the analysis cycle. All subsequent time intervals are relative to the time of sample addition. Additional cams or disc tabs, set to correspond to the elution times of components to be measured, control switches which gate bridge signals to the recorder and select attenuator potentiometers for each component of interest. The programmer also schedules the recorder chart drive and in some analyzers allows for automatic bridge zero standardization.

Process chromatographic analyzers are discussed in greater detail in recent publications (*3–5*).

Applications of Process Chromatographic Analyzers

Process chromatographic analyzers are of such recent development that few results from plant applications have been made public.

One of the publicized uses of chromatographic analyzers for on-stream analysis was by the Esso Research and Engineering Company (*2*). This analyzer, used for the analysis of propane in propylene, employs unique instrumentation. Instrument air is used as carrier gas and heats of adsorption are used to detect and measure sample components. The detector is a modification of the water analyzer developed by Esso and marketed by the Mine Safety Appliances Company. With activated carbon in place of silica used for water analysis, this detector is found to be very sensitive to low concentrations of hydrocarbons in air.

The analyzer was restricted to the use of adsorbent columns since it was thought that air carrier would oxidize partitioning agents with resultant

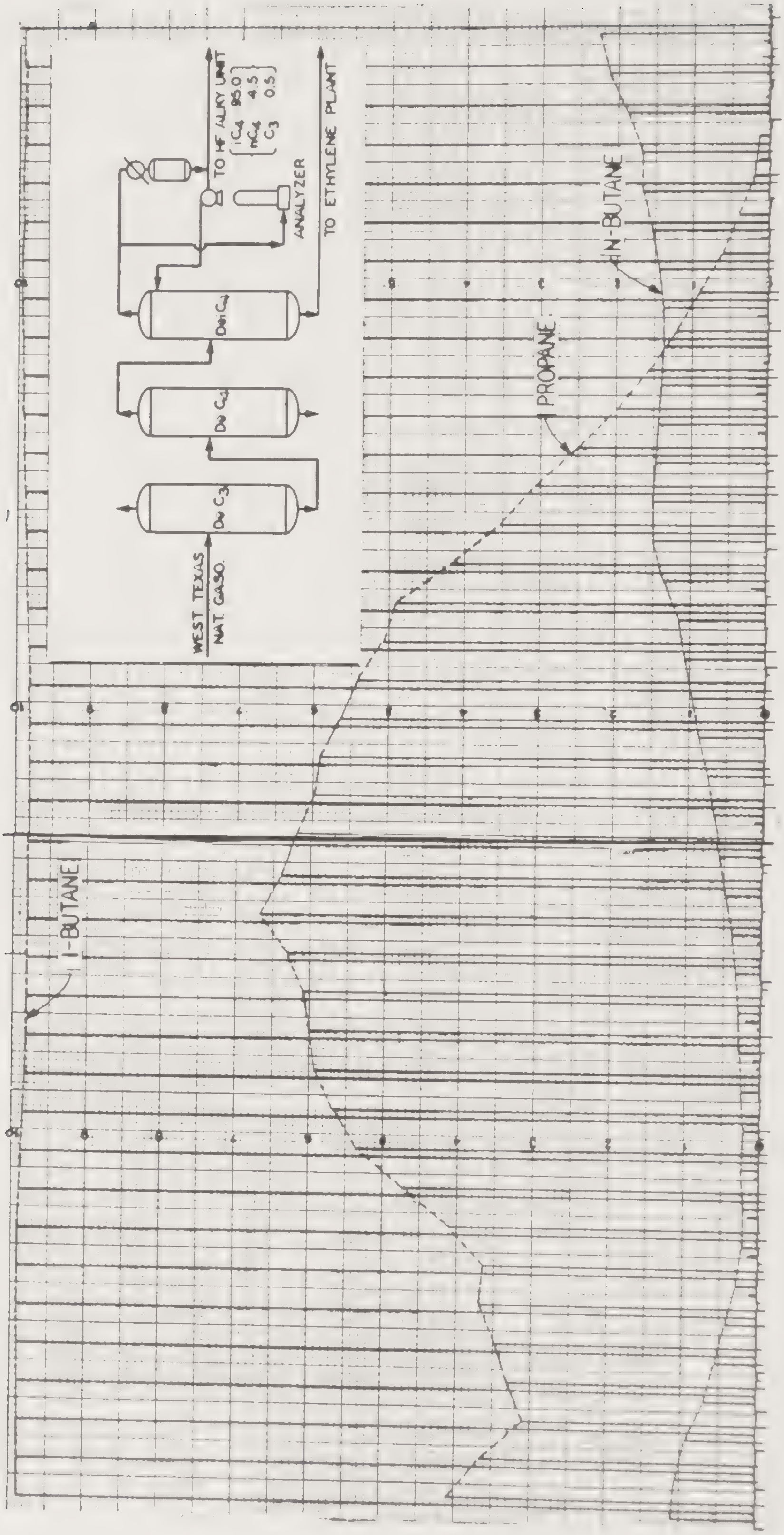

FIG. 6. Process monitoring application.

loss in efficiency of separation. A complete analysis occurs every 15 to 30 minutes with a reproducibility of ± one per cent for each component.

The versatility and utility of process chromatographic analyzers can be well demonstrated by a discussion of their application to a hydrocarbon separation unit. This unit, shown in Fig. 6, is a fractionating unit for natural gas liquids and consists of a depropanizer column, a debutanizer column, and a deisobutanizer column.

One can control fractionator product quality by controlling both the pressure and temperature of the column. More frequently, the column is adjusted to constant pressure and product quality is controlled by varying the temperature at a suitable point in the column. In a binary system, at constant pressure, temperature is a measure of the concentrations of the two components. Most fractionators, however, involve hydrocarbon separations of more than two components, and temperature becomes a multivalued function of composition. In this case, the temperature controller set point is usually reset according to periodic laboratory analyses.

In the fractionating unit, shown in Fig. 6, a process chromatographic analyzer is used to monitor the overhead product from the deisobutanizer column. High purity isobutane, 98 per cent or better, is the desired end product. The major impurities at this point are propane and normal butane.

The analyzer is set up on a 10 minute analysis cycle using an 18-foot column of Dow-Corning 200 Silicone fluid of 200 centistokes viscosity. The column contains 40 per cent by weight of liquid supported on crushed Johns-Manville C-22 firebrick. This column-packing provides the required separation and is stable at the operating temperature of the analyzer. The analyzer is set to 0–100 per cent full scale for isobutane and 0–5 per cent full scale for propane and normal butane.

The sampling system consists of a vaporizer-regulator installed at the sample point on the process stream as shown in Fig. 4. The sample line between the vaporizer-regulator and the analyzer is steam traced. A sample flow of 1000 cc per minute bypasses the sample valve to minimize sampling time lag.

The analyzer is calibrated by analyzing samples of known composition. On-stream calibration checks and span adjustments are made by comparison with laboratory analyses. Analyzer readings at the time the laboratory sample is drawn are noted. When the laboratory analyses are reported, an artificial signal is impressed on the detector bridge to give a recorder reading equal to that obtained at the time the sample for laboratory analysis was taken. The attenuator potentiometer for each sample component is then adjusted to give a recorder reading corresponding to the concentration obtained by the laboratory analysis.

Normal butane concentrations, as obtained by the analyzer, are used in the control of the butane splitter column through manual resetting of temperature at the control point. The propane concentration in the butane splitter overhead product is used to reset the temperature controller on the depropanizer column. Figure 6 shows a record obtained with this analyzer during an operating upset in the depropanizer column.

A process chromatographic analyzer on the bottoms product from the butane splitter column assists in controlling normal butane purity and yields information of value in controlling the debutanizer column. The desired product here is high purity normal butane. Isobutane and isopentane are the major impurities.

The sampling system and chromatographic column for this installation are the same as those used for the butane splitter overhead product. The analyzer is adjusted to 0–100 per cent full scale for normal butane and 0–5 per cent full scale for isobutane and isopentane. Isobutane concentration as obtained from this analyzer is used for manual control of the butane splitter column through reset of steam and reflux flow rates. The concentration of isopentane is used to manually reset the control point of a composition controller on the debutanizer column.

Thus monitoring of the composition of two product streams from this unit provides information useful in the control of the three columns. With the analyzers installed on the butane splitter column, composition data required for the calculation of material balances for the column are readily and automatically available.

Use of process chromatographic analyzers is not limited to hydrocarbon streams. There are numerous potential applications in both the organic and inorganic chemical industries.

The Carbide and Carbon Chemicals Company has reported use of a plant type chromatographic analyzer to measure chlorine purity (*8*). This analyzer gives an analysis every ten minutes with a reproducible accuracy of better than 0.2 per cent over a range of 95–100 per cent chlorine.

A second example of the use of a process chromatographic analyzer in inorganic analysis is that of measuring the hydrogen-nitrogen ratio in an ammonia synthesis plant where a hydrogen-nitrogen ratio of 3 to 1 in the recycle gas from the converters is maintained for optimum conversion. Methane, helium, and argon act as inert diluents in the process and are held below certain maximum concentrations. The concentrations of methane and argon are also measured with the chromatographic analyzer.

An 18-foot column of Linde Molecular Sieve 13X gives adequate separation of hydrogen, oxygen, nitrogen, argon, and methane. Helium carrier is used. The hydrogen concentration (approximately 60 per cent) is sufficiently large to permit determination of hydrogen in helium carrier.

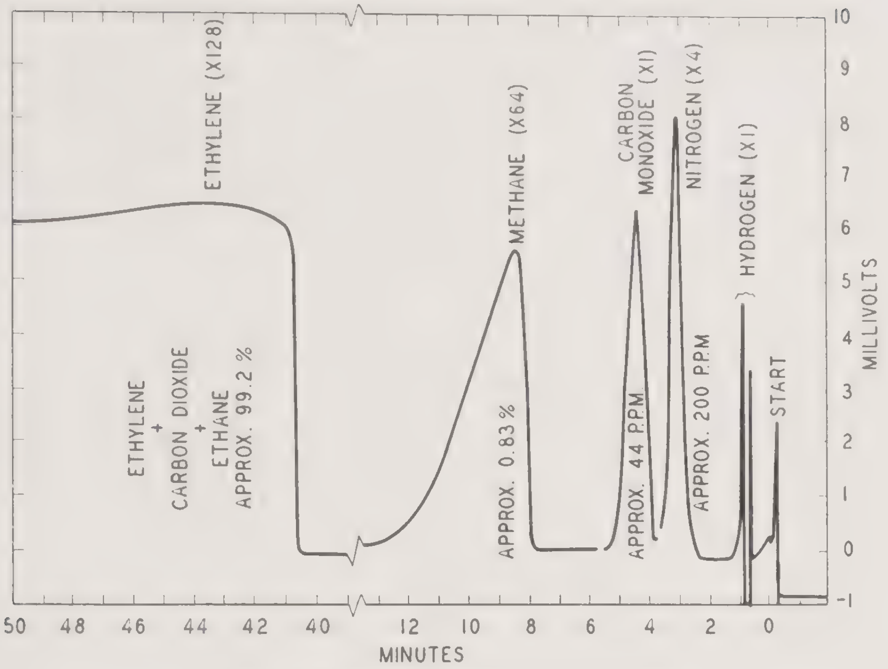

Fig. 7. Trace analyzer chromatogram.

Polarity of the signal for the hydrogen peak is automatically reversed by the programmer. The ratio of hydrogen to nitrogen is calculated from peak heights but it is relatively simple to design equipment to provide this ratio directly.

Another type of analytical problem which occurs with increasing frequency in modern processing plants is that of measuring "parts-per-million" quantities of trace impurities. Use of chromatographic techniques for such analyses appears highly attractive but standard instrumentation does not provide adequate sensitivity for such measurements. Special analyzers can be developed for such applications. Figure 7 shows a chromatogram obtained with a special process analyzer developed for the measurement of trace quantities of carbon monoxide in ethylene. The analyzer has a full scale range of 60 parts per million carbon monoxide. Six chromatographic columns are used in sequence to provide analyses at thirty minute intervals. The analyzer is entirely automatic in operation.

Application to Automatic Control

The applications of chromatographic analyzers thus far discussed can be considered control applications only in the sense that the operator closes the loop between the analyzer and the manipulated variable. The next logical step is elimination of the operator from the loop and introduction of the analyzer output signal into an automatic control system.

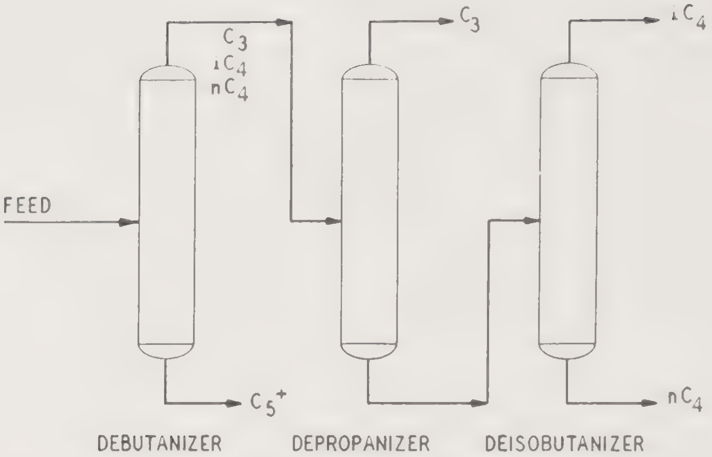

FIG. 8. Natural gasoline fractionation flow sheet.

Application of process chromatographic analyzers to automatic control is complicated by the intermittent nature of the analyzer output and the time lag in the analysis cycle. The analyzer signal must be converted to a form suitable for use with a continuous controller and with the length of analysis cycles now available (up to 30 minutes) some type of cascade control must be used.

Figure 8 shows a process unit with an automatic control system. In this process, normal butane containing less than 0.1 mole per cent isopentane is the desired product. The separation determining the isopentane content occurs in the debutanizer. Therefore it is necessary to control the

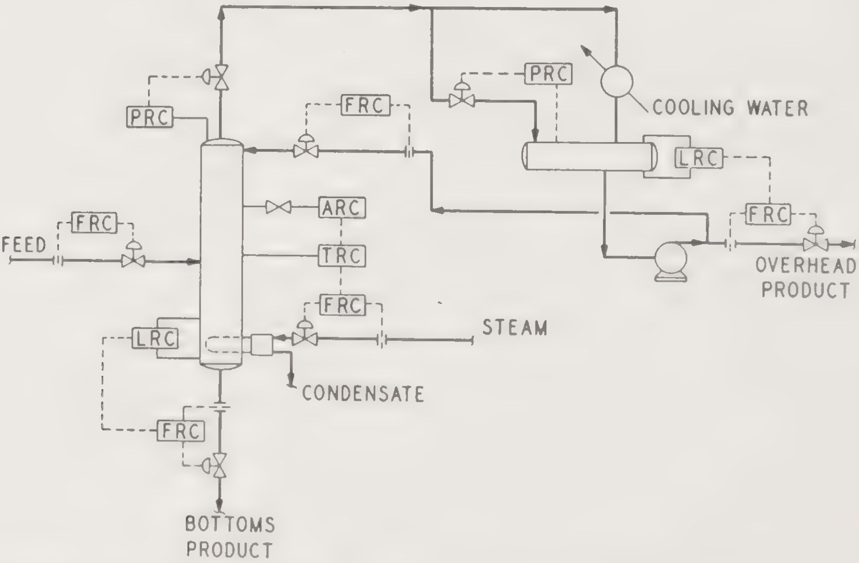

FIG. 9. Fractionation control system for controlling overhead purity with a chromatographic analyzer.

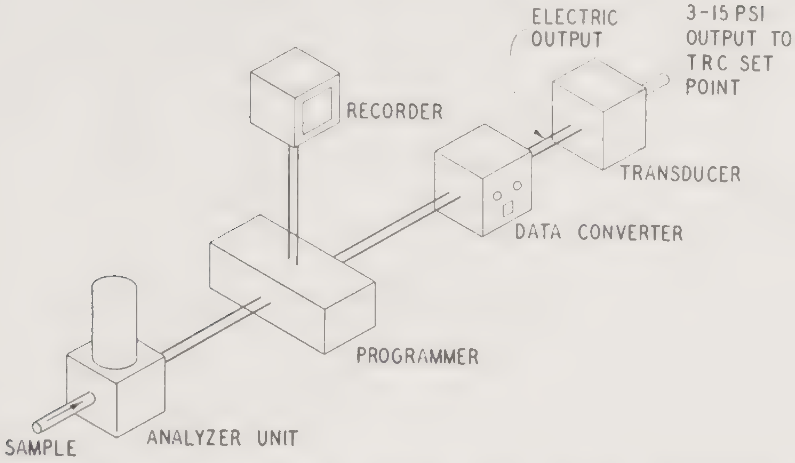

FIG. 10. Process chromatograph equipment block diagram for automatic control use.

isopentane concentration in the overhead of this column. A control system for the debutanizer column is shown in Fig. 9. The chromatographic analyzer is designated as ARC (analyzer-recorder-controller). A 3–15 psi air signal proportional to the isopentane concentration is used to reset the temperature controller set point. The temperature recorder-controller resets the flow controller in the steam line.

Figure 10 shows a block diagram of the equipment necessary to convert the analyzer output into a pneumatic control signal. The data converter may take one of several forms. Depending on the application, it may be an integrator, a ratio computer, a peak reader, or a more elaborate multichannel computer. In the present application, the converter is a peak reader which converts peak height for isopentane into a step function more suitable for a control signal. An electronic recorder is used to present the concentrations of additional components in bar graph form.

FUTURE TRENDS

It is always dangerous to make predictions in a new field of development particularly before present instrumentation is evaluated, but even at this stage, certain needs and developmental trends can be foreseen.

More rapid analyzer response is certainly desirable. Maximum cycle lengths of one minute would simplify application to automatic control. With such cycle lengths, it would be possible, in many cases, to apply analyzer signals directly to process control without resorting to cascaded systems.

Chromatographic analyzers, especially high speed analyzers, should be ideally suited for the optimization of processing units through computer control. For the natural gasoline separations unit of Fig. 6, four chromatographic analyzers can provide all the data on stream composition required for computer control of the unit. Composition data and signals from the measurement of other process variables will be fed into computers which will perform the necessary computations and adjust the process variables for optimum operation. It should be emphasized that four analytical instruments are sufficient, in this application, only because they are multicomponent analyzers.

Successful application of computer control cannot be accomplished until the dynamic properties of a system have been thoroughly studied. Process chromatographic analyzers can play an important role in making these studies.

Another field for development arises from the need for improved forms of data presentation. Even when information from chromatographic analyzers is fed into automatic control systems, visual presentation of data is desirable and is necessary for manual operation in the event of failure of the automatic control system.

High speed chromatographic analysis will almost certainly preclude use of some of the present methods of multicomponent data display. Bar graph presentation would be extremely wasteful of chart paper and present storage problems. Standard recorders are too slow for high speed bar graph recording. Bar graph presentation can be retained, where desired, by recording the concentration of only one sample component per analyzer cycle (or every nth cycle) until all components have been recorded.

A more desirable form of data presentation would be the continuous recording of each sample component, either on a single chart with distinctive color coding or with a separate recorder for each component. For such recording, it will be necessary to convert the output from the analyzer into a continuous signal. This can be done with integrating or peak reading mechanisms plus some type of memory or holding device.

Process chromatographic analyzers must be able to handle high boiling liquid samples. This is largely a problem of accurately metering small quantities of liquid samples. One possible solution to this problem is vaporization of the sample and heating of the sample addition system up to the inlet of the column. An alternate method is that of sampling under reduced pressure. Both of these methods are limited and a new technique for the accurate and automatic metering of high boiling liquid samples is needed.

There is a need for a process chromatographic analyzer which will be generally applicable to the determination of "parts-per-million" quantities of volatile impurities. The trace chromatographic analyzer previously discussed is of limited applicability for analyses of this kind.

Perhaps chromatographic analyzers can be extended to trace analysis through amplification of the detector signal, through the development of more sensitive detectors or the use of more specific detectors. Even with adequate detector sensitivity, a trace component eluted with a diffused band of a major component is difficult to measure. In some cases, this difficulty may be overcome by use of the major sample component as carrier gas. However, this results in an enormous loss in sensitivity when thermal conductivity detectors are used.

An alternate approach to the development of a chromatographic analyzer for trace analyses is that of concentrating the impurities from a large quantity of sample. To be entirely satisfactory, this analyzer should be capable of concentrating a large variety of impurities from a wide range of major sample components.

Another interesting possibility is that of designing a truly continuous (as contrasted to cyclic) process chromatographic analyzer (*1*). Perhaps our thinking has been conditioned by close association with other types of continuous analyzers and this step is not desirable. Certainly, to build a continuous chromatographic analyzer without, at the same time, realizing an appreciable decrease in instrument response time is of no advantage. Moreover, to obtain an analyzer with a continuous signal output for only one sample component would cancel the principal advantage of chromatographic analyzers: complete compositional analyses of process streams.

An important consideration in the future development, not only of chromatographic analyzers but of all process analyzers, is that of appearance and neatness of design. It appears that the more harmoniously an analyzer fits into the plant environment, the more readily it is accepted by operating personnel and the more reliance is placed in its operation. Perhaps this indicates that analyzers should be designed, at least externally, to have more of the rugged appearance of ordinary plant equipment.

Analyzers should also be designed to operate satisfactorily under widely varying ambient conditions so that they can be moved out of instrument houses and back into the processing areas where they properly belong.

The acceptability of process chromatographic analyzers can be further improved through miniaturization. Most mechanical components of these analyzers can be reduced in size and the entire unit enclosed in a smaller explosion-proof housing.

CONCLUSION

Chromatographic analyzers offer a number of advantages as instruments for use in monitoring and controlling chemical processing operations. These analyzers are widely applicable, relatively inexpensive, and can automatically provide complete compositional analyses of process streams. To date, their principal disadvantage appears to be the time required to complete an analysis cycle.

Initially, these analyzers will be confined primarily to process monitoring applications, but it should require only a few years to bridge the gap to automatic control. The development of process chromatographic analyzers may prove to be a major step toward full automation of processing operations.

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Discussion

Fuller (*The Foxboro Company, Massachusetts*): On your last slide, have you any idea as to the life of that silicone-filled column under the continuous conditions that you mentioned here—frequency and high temperature?

Ayers: No, we have had this particular analyzer in operation for approximately 9 months with very negligible changes in either retention time or span.

Fuller: In other words, life is certainly greater than 9 months.

Ayers: Yes, it is at least as great as 9 months.

Lewis (*Tennessee Eastman Company, Tennessee*): Do you, or does anyone here, know of a precise way for automatically sampling from a liquid stream and injecting the liquid sample into a chromatographic column?

Ayers: If someone here does have the answer to that, I would appreciate learning it myself. It is certainly one of our big problems.

Skarstrom (*Esso Research and Engineering Co., New Jersey*): I know of a company that manufactures a sampler which if you have a liquid flowing in the stream and you want a representative sample of this liquid over a course of a day, say, it collects this representative sample. It is made by a firm called Gilbert and Barker who are known chiefly for their manufacture of gasoline pumps. This device collects a little tiny squirt every so often, depending on how you set up a little multivibrator that operates a piston. I think very likely that this device could be adapted to taking liquid samples, including liquids with entrained gases.

Ayers: I would also like to say that we do sample liquids, but of course this is limited to those streams which can be vaporized at, say, less than 100 degrees Centigrade.

Kirkland (*E. I. du Pont de Nemours & Co., Inc., Delaware*): Is the limitation here one of being able to sample very small liquid samples with high precision?

Ayers: Yes, that is what I was referring to.

KIRKLAND: What would be the objection to sampling a very large, say $\frac{1}{2}$ cc, sample from the stream and using a very large sample column?

AYERS: This is done frequently. There are a number of advantages, however, in using smaller columns. One of them is that you can get somewhat better resolution if you don't go to too large a column diameter. Another is, of course, in the miniaturization of equipment. These advantages would certainly be nullified by using a large column. We may have to take such an approach, however, if we can't find better methods for measuring small quantities, say microliters, of liquid sample.

NOEBELS (*Beckman Instruments, Inc., California*): Buell, what experience have you had in complicated streams? In other words, the most complicated that you have shown on the board has gone up to about a C_5. Have you gone any higher, and how do you reduce the emergence time with good resolution if you have?

AYERS: I am glad that you asked that, Hank, because of one point that I had meant to bring out and forgot. We have naturally started out with these process analyzers on some of our simpler streams. We are working on more complicated streams, but we, as yet, have not had any actual application experience with them.

NOEBELS: I might also perhaps interject a little bit of our own experience there. We have worked with quite a number of complicated streams and have used a split column technique to diminish time and increase resolution of those components that normally come through on a longer time basis; also, to separate, say, oxygen and nitrogen where you might want to use a molecular sieve yet you have so many other things with it. This is accomplished by interposing a valve between two columns and actuating it at the proper time. You can overcome a lot of these difficulties.

COATES (*The Perkin-Elmer Corporation, Connecticut*): The question with respect to increasing sample size by increasing column diameter—I believe there is one further disadvantage which should be mentioned here. The increased consumption of carrier gas would undoubtedly present a problem.

SKARSTROM: I would like to pose a rather difficult problem for the widespread use of these instruments; that is the helium carrier gas. Companies that normally operate with automatic control usually run continuous processes. There is a problem at time in the availability of helium. It would be quite disastrous if an instrument were to go out of commission because of the company's inability to obtain a bottle of helium. I believe that the people who are looking into chromatographic analyzers for process units should consider using, say, bottled nitrogen or hydrogen, or other easily obtainable gases. This, of course, is particularly true for those companies who wish to use these instruments in foreign countries where helium is certainly not readily available.

AYERS: I believe one answer to this problem is, as was pointed out by Dr. Martin last evening, that perhaps some of the newer ionization types of detectors can operate very well on carrier gases other than helium. An alternate approach, of course, would be to design our apparatus to use smaller quantities of helium. This seems to be entirely feasible.

ANONYMOUS: Do you have any trouble with zero drift in the detectors?

AYERS: Yes, we do have trouble with zero drift at times.

CHAPTER XXVI

The Practical Design of a Vapor Fractometer for Automatic Multicomponent Analysis of Process Streams

CHARLES C. HELMS AND H. NEWELL CLAUDY

The Perkin-Elmer Corporation, Norwalk, Connecticut

INTRODUCTION

In designing a new analytical instrument there are certain fundamental criteria the instrument engineer must apply to produce a successful product. I would like to discuss both the general design criteria for analytical instruments and the way the Perkin-Elmer Corporation combined these with a rather unusual "interim" instrument testing program to evolve a final design for a process vapor fractometer.

The rapid growth, simplicity, and versatility of gas chromatography as an analytical tool in the laboratory suggested early that this method would be very useful for process stream analysis as well. With this thought in mind, an explanatory development program was begun by constructing ten process analyzers of a very simple design. These ten "interim" analyzers were purchased by customers interested in investigating the application of gas chromatography to their own particular process problems, and who cooperated by sending on information about the operation of the analyzers and various suggestions for improvements or changes which they felt would be desirable. At the same time, design work was begun on an advanced model of the analyzer. This design was based on the general criteria mentioned and on the experience gained in construction and application of the ten interim instruments. It was also continuously modified as information and suggestions came in from the field from users of the interim instruments. The net result was the final design of the Perkin-Elmer Model 184 Process Vapor Fractometer.

It should be interesting to consider briefly the general principles which guide an instrument engineer in designing equipment, and to use the Model 184 to illustrate the practical application of these principles.

GENERAL DESIGN CRITERIA

First, there are the general requirements common to all instruments. Accuracy, reproducibility, and reliability are chief among these, for unless an analyzer can consistently produce meaningful results it is worse than useless. The physical principles on which the analyzer operates impose the need to maintain certain parameters constant within very close limits.

Yet they must also be variable so that the inherent versatility of the method will be limited by inability to change to a new set of conditions.

Process instruments also have their own special requirements. They usually demand even a greater degree of stability and dependability than laboratory analyzers. Plant instruments must therefore be ruggedly constructed to withstand occasional abuse, must require only a minimum of attention and maintenance, and must be simple to service or repair. They must operate over a rather wide range of ambient temperatures. They must usually be explosion-proof or at least explosion-resistant, and most users prefer them to conform to the Class I Group D specifications.

Of course, a process instrument must be completely automatic. Size of the equipment—particularly the portions mounted on the control room panel board—is important. Finally, all controls and the data presentation used should be so simple that plant employees unfamiliar with this type of instrumentation can easily understand and use them.

Now let's take a look at the Model 184 Process Vapor Fractometer to see how these criteria were applied in its design.

DESIGN OF THE MODEL 184

Figure 1 shows the three units of the Model 184—the analysis unit in a standard explosion-proof dome, the programmer, and the recorder. The

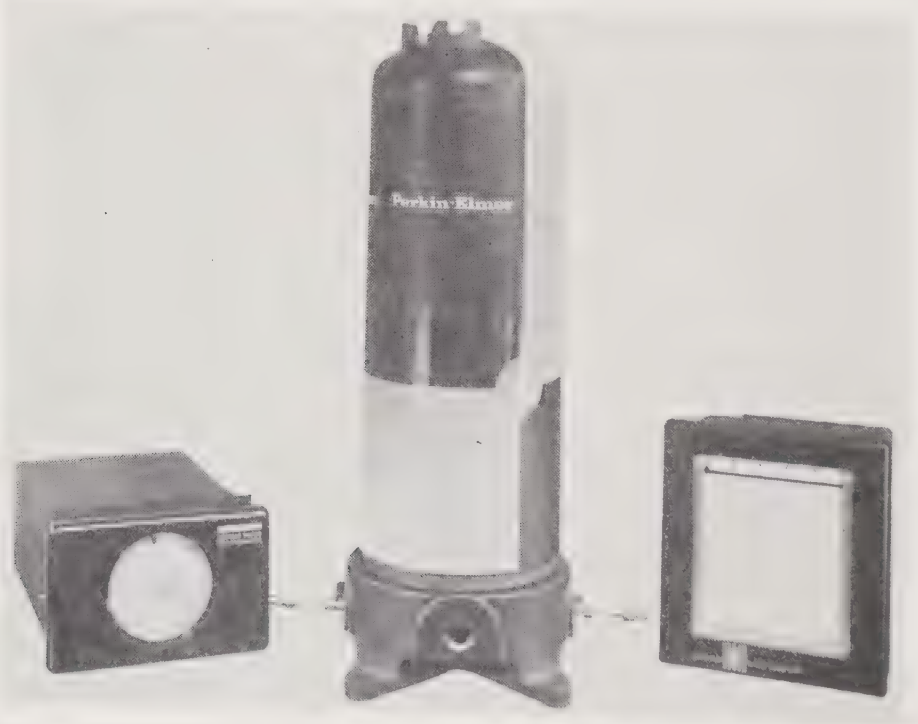

FIG. 1. Programmer, analysis unit, and recorder of the Model 184 Process Vapor Fractometer.

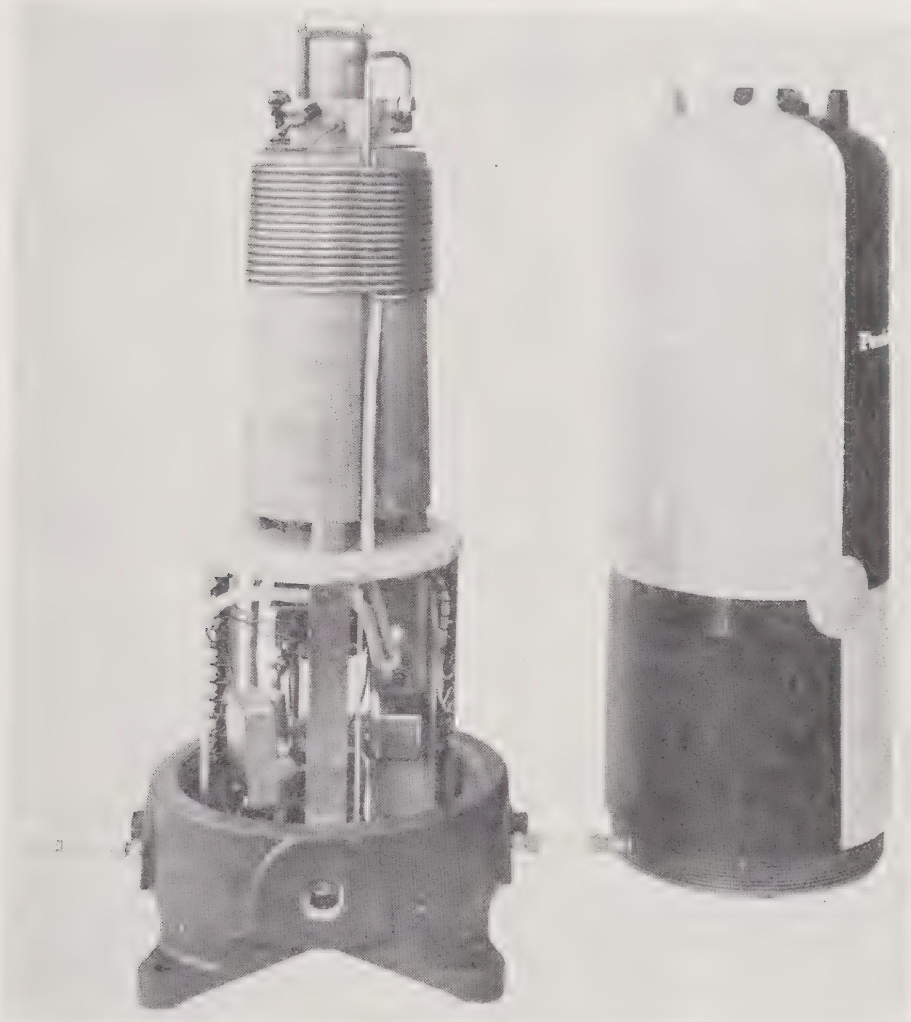

FIG. 2. Analyzer with dome removed.

analysis unit contains the column, detector, sampling valve, and the associated equipment for the gas flow systems and the temperature control. The programmer is the "brain" of the unit and controls its operation as it repeatedly analyzes the process stream. All controls the operator will use are located in the programmer. The recorder is a standard unit with slight modifications to permit the programmer to start and stop the chart drive.

Figure 2 shows the analyzer with its protective dome removed.

The thermostatting arrangement is both simple and effective. All thermostatted parts are in direct contact with an aluminum mandrel whose temperature is controlled to a tenth of a degree Centigrade. The mandrel is hollow, and within it heat exchange coils for the sample and the carrier are wound. The sensing element of the thermostat system is a mercury-in-glass thermometer with electrical contacts; power to the heaters which are built into the mandrel is switched by a thyratron-relay circuit. A second temperature control circuit with larger heaters which cut out at slightly under the thermostatted temperature is provided for quick warm-up of the unit. Alternate thermometer elements can be used to select an operating temperature in the range from 50 to 100 degrees Centigrade. Ambient temperatures may vary from minus 10 to plus 115 degrees Fahrenheit without affecting an analyzer temperature of 50 degrees Centigrade. Higher ambient temperatures are tolerable when higher thermostat temperatures are used.

The mandrel is large enough to accomodate a quarter-inch column 50 feet long.

Division of the components within the dome allows the equipment in the lower portion to operate at a lower temperature than the thermostatted portion. This contributes to increased life of the electrical components and further simplifies the thermostatting system.

The detector and sampling valve are both part of the same assembly, shown in Fig. 3. The detector is of a modified type in which there are two separate flowing streams, one the column effluent which flows through the measuring cell and the other a reference stream of helium which flows through the reference cell. This reference stream of helium is controlled by a restricting valve built into the block. Both cells are of the same configuration and vent to a common outlet. Thus both are subject to the same pressure. This has been found to enhance the stability of the detector. The detector elements are high-resistance thermistor beads.

The detector bridge power supply is a regulated Zener diode rectifier operating from line voltage and is constant to plus or minus five-hundredths of a per cent.

The sample metering valve (Fig. 4) is enclosed in a sealed, removable metal cover. Effluent from the thermal conductivity cells passes through this cover before being vented. There is thus a constant helium purge around the sample valve shown in Fig. 5 with the cover removed; should leakage ever occur there can be no build-up of explosive vapors inside the analyzer dome. The valve itself is similar to the rotary valve used in the Perkin-Elmer laboratory vapor fractometers. It is turned by a reversible motor located in the cool lower portion of the dome. It operates dry, eliminating the problem of adsorption of sample components in lubricant which degrades elution peak shapes, and also avoiding the necessity for periodic lubrication. Sample volumes are determined by a suitable length of eight-inch tubing which is connected by fittings and can easily be changed to one of different volume.

Now, how does this design conform to the criteria we discussed earlier?

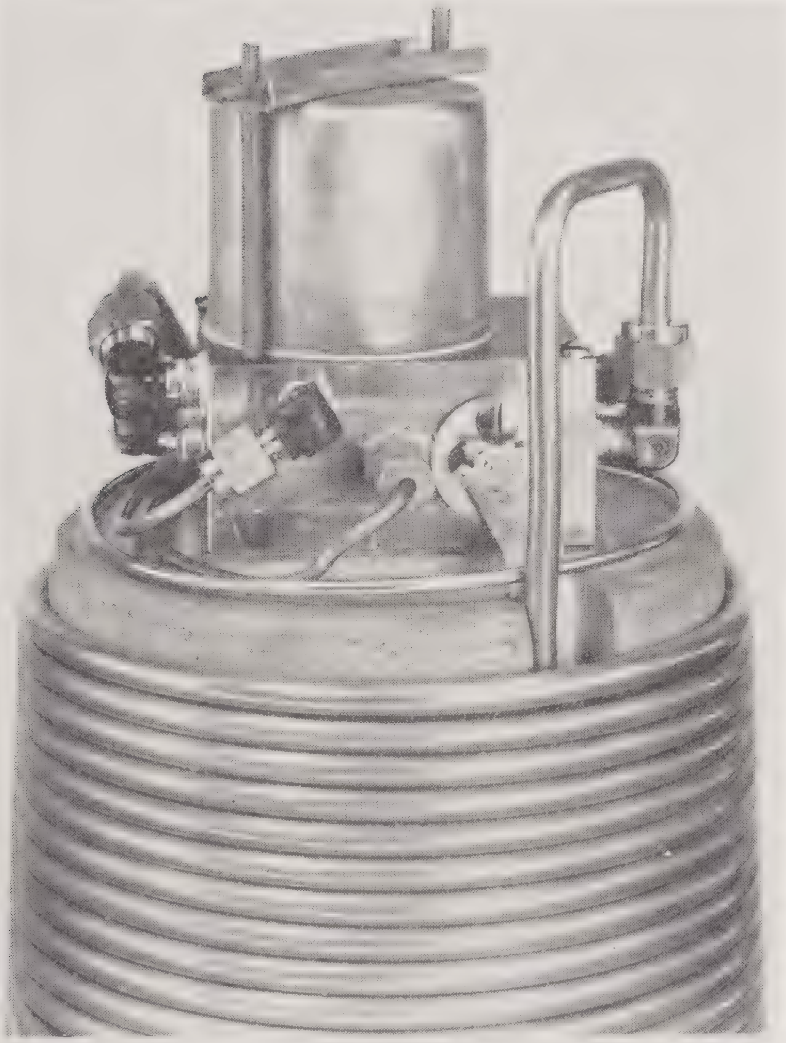

FIG. 3. Detector and sampling valve.

First, constancy of operating conditions is assured through careful regulation of all operating variables. Detector stability is enhanced by the parallel-flow system used. Second, maintenance is reduced by use of components requiring no regular periodic attention and by operating these components under conditions contributing to maximum life. Attention to safety is shown in the use of an explosion-proof enclosure for the entire assembly and in the purging arrangement provided for the sealed sample valve.

Finally, the basic design provides for flexibility in the use of the analyzer; columns, flow rates, sample volumes, and operating temperature can be easily changed.

The simplest way of achieving automatic operation in a series of repeti-

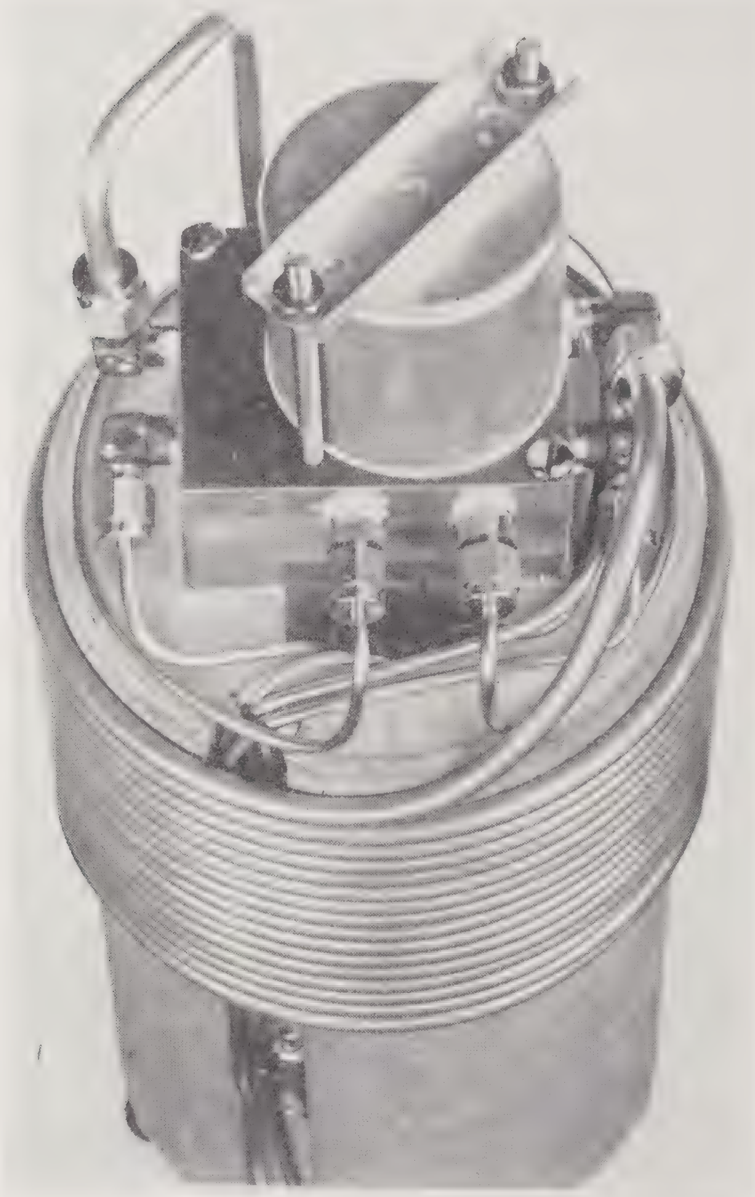

FIG. 4. Sampling valve assembly.

tive cycles would be to use a standard cam-and-switch timer to periodically actuate the sampling valve, with additional switch cams to provide several different attenuation factors. Modification of the recorder operation to draw bar charts conserves chart paper and enables the operator to see a number of previous analyses so he can keep track of trends in component concentrations.

The interim analyzer we built had a timer just about this simple. But one of the results of the interim program was the realization that some users

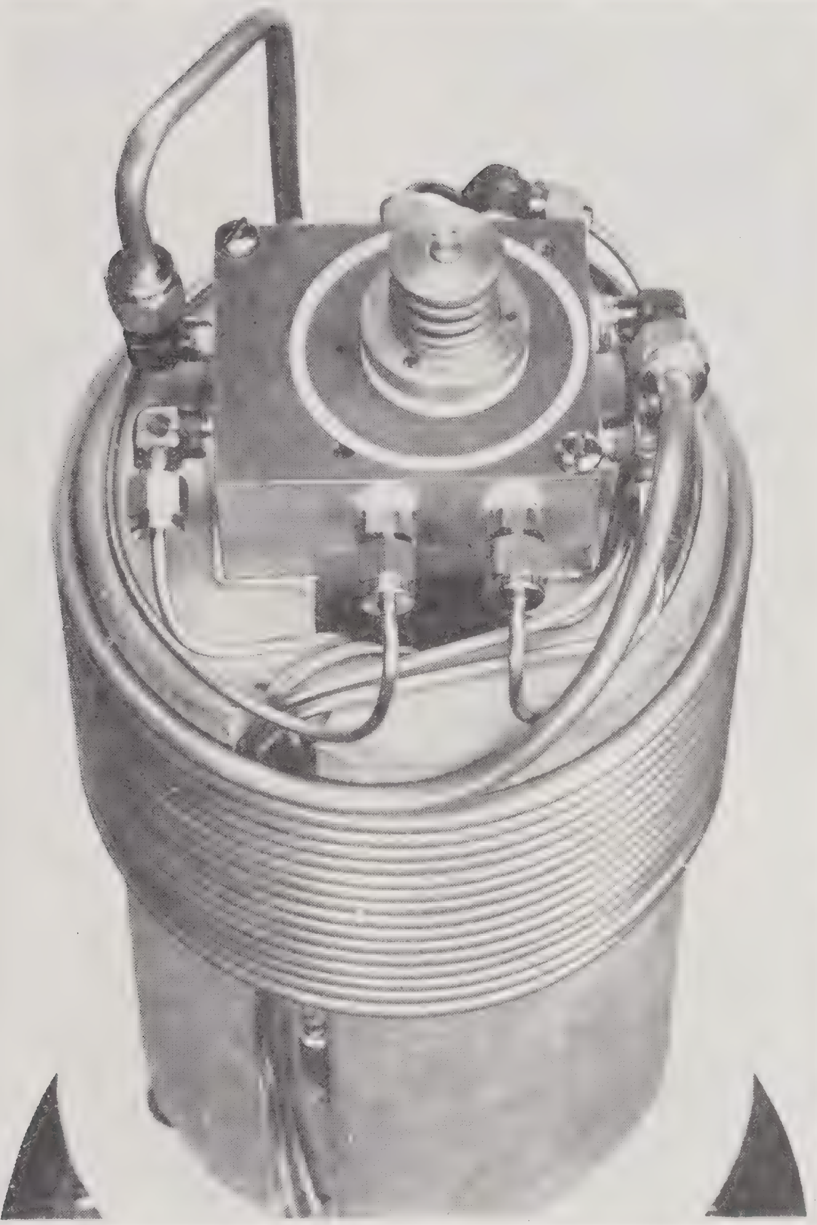

FIG. 5. Sampling valve with purge cover removed.

didn't particularly like the multiple-cam timer. They found it was inconvenient to set all the cams—there were 15—and in addition they wanted some way of indicating what part of the analysis cycle the analyzer was on. As a result of these suggestions, Perkin-Elmer developed the timer—or programmer—which is now used with the Model 184.

This programmer, shown in Fig. 6 is much simpler than the multiple-cam type it replaces. It has one master timing disc which is always visible

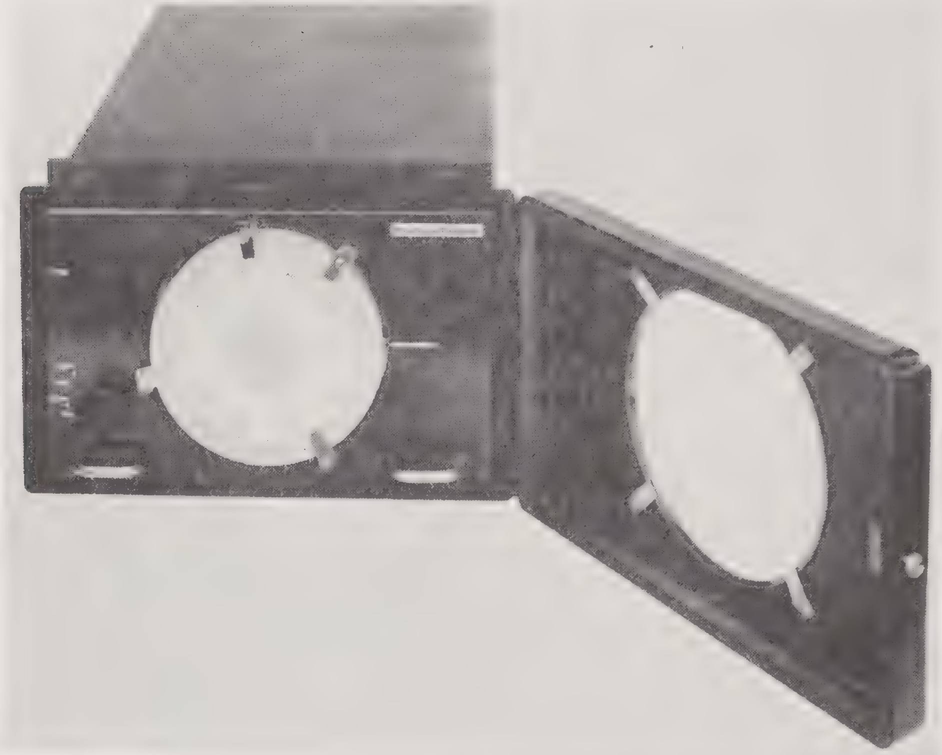

FIG. 6. Programmer with door open to show timing disc and controls.

to the operator. Attached to the disc are four movable arms. Each one represents one component of the mixture being analyzed and corresponds to an attenuation factor for that peak which is continuously adjustable from 0 to 100 per cent of detector output. The position of the arm on the dial corresponds to the elution time of the component. A separate and independent adjustment determines the length of time that the recorder looks at each peak. At other times the recorder input is shorted and the indicator is at zero. During these intervals the programmer automatically advances the chart so that it is ready to record the next peak. The record consists of groups of up to four lines, each one representing a selected component of the mixture being analyzed. An additional chart space separates the consecutive analyses. The independent attenuation settings permit variation of the effective sensitivity of the detector so that the height of each peak—that is, the length of the line—can be made to read directly in per cent concentration of the component on the recorder scale, with an appropriate scale range, such as 0 to 1, 0 to 50, or 0 to 100 per cent, for each component.

A second point we discovered in the interim program was the fact that most users wanted to have an automatic zero adjustment. Zero drift is very gradual if it occurs at all. But providing an automatic correction eliminates an adjustment which the operator would otherwise have to make. So at the end of each cycle, the recorder is connected to the detector output at maximum sensitivity and a simple contact arrangement on the recorder energizes a servo motor which turns a zero balancing potentiometer to produce a true zero bridge output.

In addition to the normal bar graph recording of component concentrations, other modes of operation are available. One provides a standard fractogram showing all peaks. This permits use of the Model 184 as a conventional chromatographic analyzer, so that it can perform a complete analysis of the process stream. Another operating mode combines these two, so that the chart runs continuously but displays only the pre-selected peaks. This is the "check timing" mode, and permits verification of the timing set-up. Finally, a fourth mode connects the attenuators, one by one, to a test signal which can be varied to duplicate a detector bridge output signal. This is useful for calibration. For instance, a fractogram analysis of the process stream may indicate that a previously recorded peak should have been 30 instead of 32 chart divisions high. The test signal is switched to the attenuator in question and adjusted until the recorder pen is at 32. The attenuator is then changed to give a reading of 30, correcting the calibration of the analyzer for that peak.

The test signal may also be used to set the attenuators in exact relative ratios for convenience in making fractogram analyses, or to determine the relative ratios at which they have been previously set.

These four modes of operation are selected by a switch located on the inner panel of the programmer. The other knob on this panel is a coarse zero adjustment.

Now let's look at the programmer in detail to see how the design criteria we've been talking about apply to it.

We've already covered the simplified automatic operation. Ordinarily no attention from the operator is required. Any malfunction will usually be apparent from the chart record, but it may be desirable to make a check timing run once a week or so, and perhaps a calibration check using a known mixture fed to the analyzer, the results of a laboratory analysis on the plant stream, or an analysis run in the fractogram mode by the Model 184 itself.

A closer look at the programmer removed from its case (Fig. 7) shows that there are no exposed switch contacts. All switching is done with hermetically sealed mercury or magnetic switches, mercury for the power circuits and magnetic for signal circuits. This is important from the standpoint of safety, because it means elimination of exposed contacts which might spark and ignite combustible vapors. Contact corrosion is also eliminated.

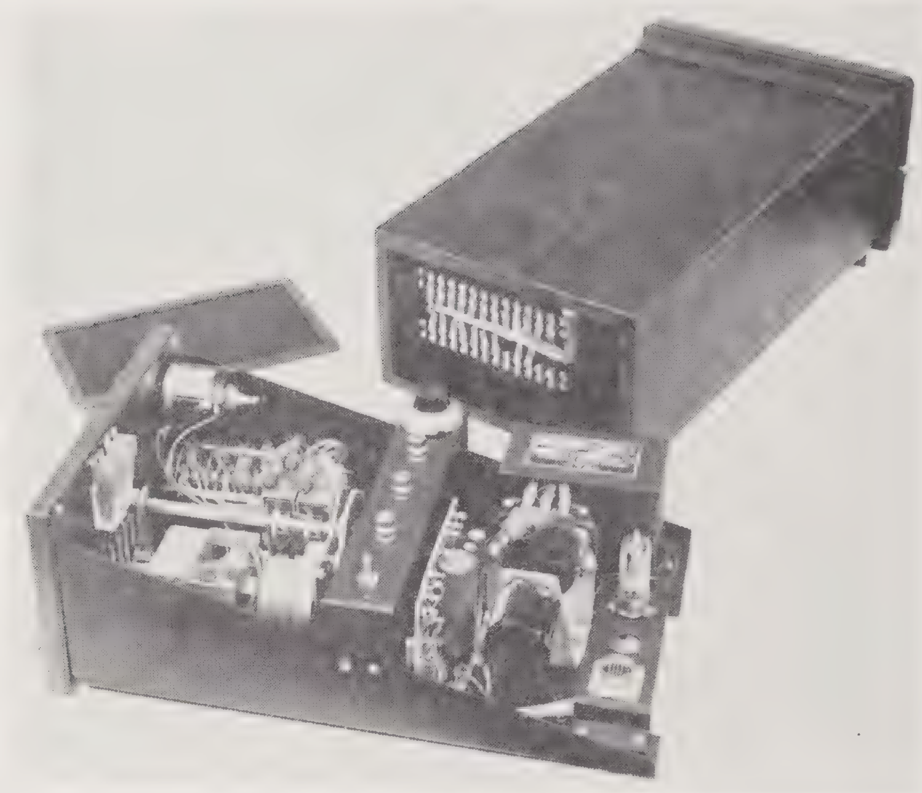

FIG. 7. Programmer removal from its case.

Located on the rear portion of the programmer chassis are the zero adjusting motor and potentiometer and the detector bridge power supply.

The attenuator potentiometers and the test signal adjustment are placed inside the programmer to conserve front panel area and to protect them from being inadvertently disturbed.

Cable plugs and flexible cable are used to connect the programmer chassis to terminal boards accessible from the back of the programmer case. The programmer slides in and out of its case so that its operation can be observed while it is actually running.

Independent outputs are provided on the terminal boards for each of the four component peaks, so that, if desired, extra recorders can be used for each peak. This opens up the additional possibility of selecting one peak output for use in a closed-loop control system.

Size of the programmer has been reduced to the minimum consistent with convenient placement of parts. It occupies a panel space only seven inches high and eleven inches wide. These dimensions conform to those of standard small-size potentiometer recorders so that the panel board installation will be convenient.

CONCLUSION

The approach taken with the interim instrument program admittedly required a greater time to put an improved second-design instrument into production. But the final result of the direct cooperation between users and manufacturer should certainly be of benefit to both.

Acknowledgment

I should like to express the appreciation of the Perkin-Elmer Corporation to the purchasers of our interim instruments who contributed so much in the way of criticism and suggestions. Particular thanks are due to members of the Instrument Development Division of Phillips Petroleum Company under the leadership of Tom Wherry and Frank Karasek. Perkin-Elmer has been privileged to work with them in a joint development program on chromatographic analyzers during the last twelve months. The advice of Ben Thomas of the Texas Butadiene and Chemical Corporation was also invaluable. To these people, and to all the others who gave us the benefit of their experience in the process analyzer field, we are most grateful.

CHAPTER XXVII

Exploratory Process Gas Chromatography

T. L. ZINN, W. J. BAKER, H. L. NORLIN, AND R. F. WALL

Monsanto Chemical Company, Plastics Division, Texas City, Texas

INTRODUCTION

Interest in process gas chromatography at Monsanto led to the determination of several design parameters and operating conditions that were considered best and/or necessary for process instruments. These proved to be a guide for process applications of chromatographs, and are discussed below.

INSTRUMENT

The instrument consists of a thermistor type thermal conductivity cell, a thermostated air bath for detector and column, a rotary 6-way valve, and normally a ¼ in. diameter column. Design was kept as simple as possible, as shown in Fig. 1. For process applications a programing unit was found necessary to adjust to several ranges of sensitivity for ease of calibration to the several components in the stream. Experience has indicated that an automatic zero is usually essential, particularly in applications requiring high sensitivity. Almost every process stream has a minor component of interest which requires high sensitivity.

Thermistors

Thermistors have been used exclusively because of the sensitivities required. They made possible high sensitivity without voltage amplification or microvolt recorders. Average life has been from 6–12 months with cause of failures generally unknown. The replacement was not considered overly troublesome.

Air Bath

The air bath employs a conventional blower and heater usually with a bi-metal thermostat. A precision ±0.1°C thermostat is used for high sensitivity applications. Some insulation of the column and detector and addition of thermal mass makes the bi-metal thermostat adequate except for the most sensitive applications. Direct heating of the detector and column block appears to be simple but time was not found to explore this approach. A continuously adjustable thermostat has been found very desirable

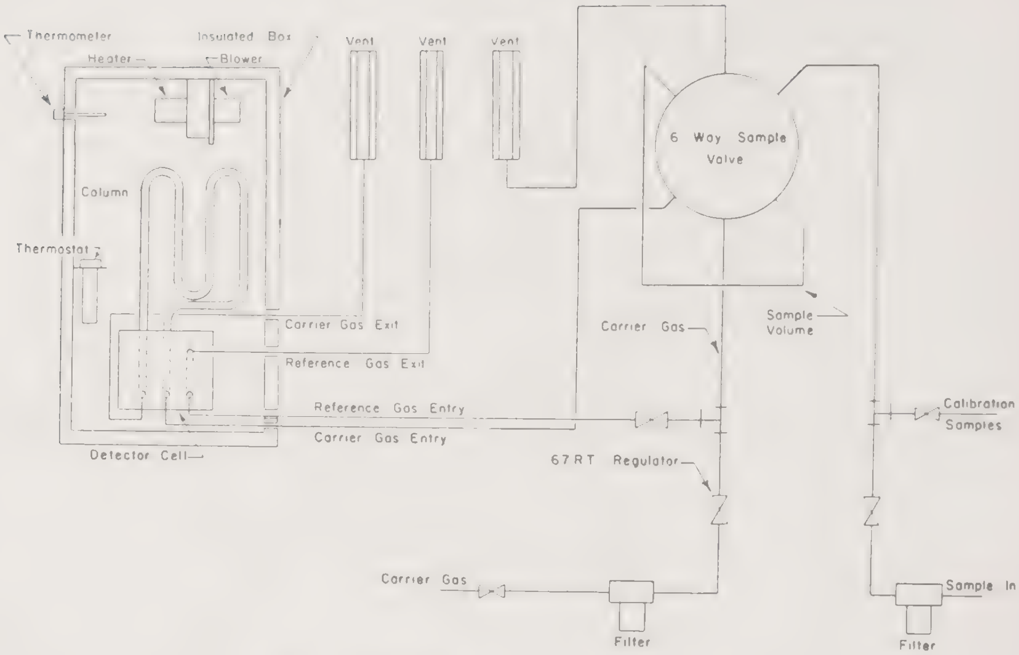

FIG. 1. Schematic of gas chromatograph.

to allow elution time adjustment to compensate for column aging. Thermostating the column and detector together was the simplest procedure, and well suited to process chromatographs.

Sample Valve

The sample valve is a conventional 6-way plug valve as shown in Fig. 2. This type was chosen because it requires less precision of construction.

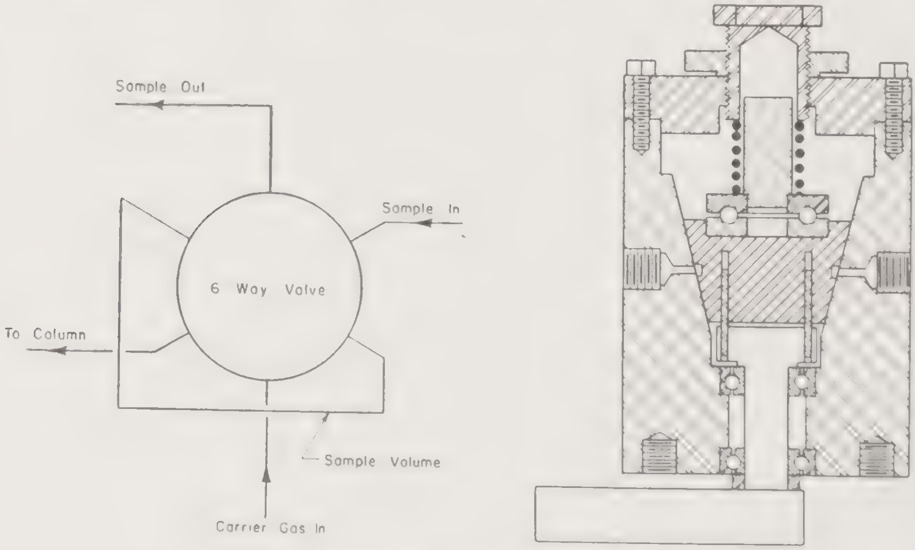

FIG. 2. Six-way sample valve.

The floating plug allows self alignment and the ball bearings were found necessary for long life.

Columns

Columns of ¼ in. tubing were used following general practice. Later exploration indicated that ⅜ in. tubing gave almost equal resolution, was easier to pack and had less pressure drop so that the sample valve could be operated under lower pressure with less likelihood of leaking. No significant differences were observed between straight, spiral, or hair pin columns. The hair pin column is compact and is preferred because it is easy to form. Stainless steel columns were used when the sample stream was corrosive. The use of copper or aluminum is preferred where possible because stainless steel is difficult to form.

Flow System

The flow system employed is indicated in Fig. 1. The bypass to the reference thermistor results in less signal noise with valve actuation than when the reference thermistor is located at the elevated pressure in the carrier stream ahead of the valve. Experiment has shown that long tubes between column and detector, bends, right angles, and tee's have little effect on resolution. The conclusion was that close streamlined coupling is not necessary. Reasonable care with standard fittings is adequate.

Thermistor Location

Figure 3 presents the results of a study of thermistor position in a 3⁄16 in. diameter carrier stream. With regard to peak symmetry and sensitivities the position of the thermistor is not critical. A 50% increase in resolution is obtained in moving from the edge to the center of the flow path. It is concluded that reasonable care should be taken to locate the detector in the center of the flow path.

Recording

Recording of the peak height in a process chromatograph appears to be the practical method of measurement. If the instrument stability is not adequate to allow use of peak height, then on a long term basis, with presently available equipment, the application is not considered practical. Nonlinearities resulting from peak height calibration have not warranted area calibration. While bar graphs offer advantages in data presentation they are not justified on the basis of chart paper saving alone. They offer complication in programing and fail to record seldom occuring new components that might be detected by the conventional chromatogram.

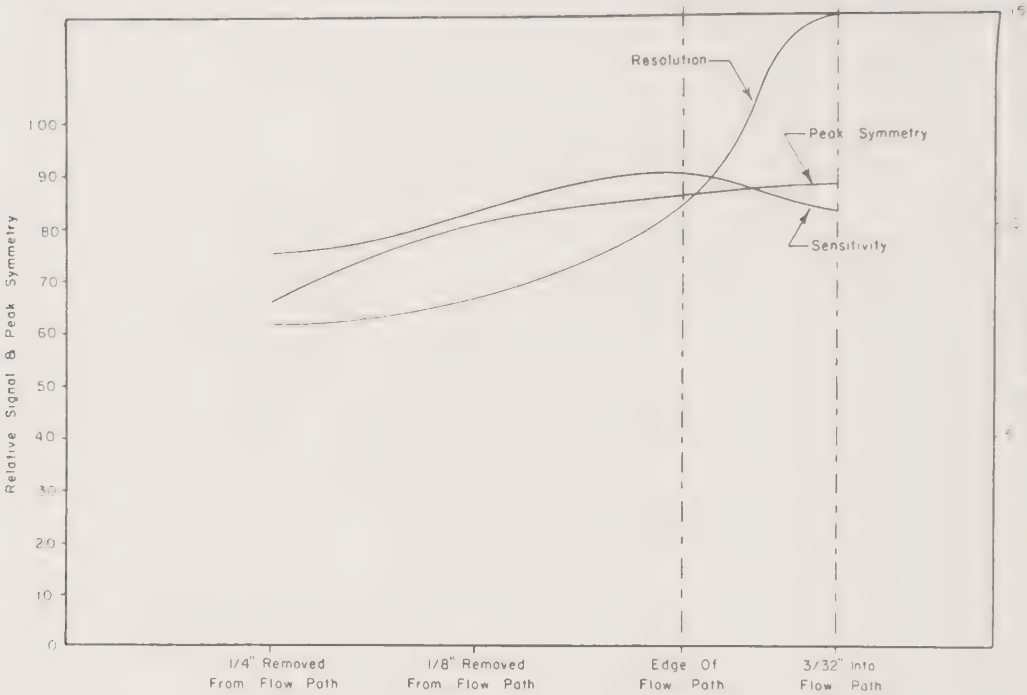

FIG. 3. Thermistor position study.

PROCESS EXPERIENCE

Experience in applying chromatographs to streams indicated some general desired design and operational characteristics. Specific column development will not be discussed, for each stream requires a column adopted to that particular problem. Adsorption columns are used for light hydrocarbons. However, pure adsorption columns tend to load with heavier materials often found in a process stream and the resultant change of elution time causes calibration and programing problems. The use of 1 to 3% heavy oil pre-loading of these column has eliminated most of these difficulties while retaining most of their adsorption characteristics.

Columns requiring operation below 110°F are at the present time impractical for field applications in the Gulf Coast Area since this is the minimum practical thermostating temperature. Particular attention must be given to the volatility of the liquid phase of columns used in process instruments. Some that are quite usable in the laboratory will tend to drift in plant use.

Attention must be given to the change of elution time of peaks with change of relative concentration of major stream components due to the change in the nature of the column at equilibrium with these components. The effects of water are particularly bad, and even though apparently eluted in the program period, a considerable effect on elution time and hence on calibration and programing may occur. Adsorbed polar compounds can be expected to change the nature of the packing surface.

APPLICATION TECHNIQUES

The following techniques are advisable to obtain maximum reliability.

Sample

Overall analytical instrument performance cannot be better than the sample system; therefore, consider the requirements carefully and do the job thoroughly. The sample system should employ adequate filtering, i.e., 0.1 micron filters, and removal of condensables or drying, as required. It may be necessary to heat sample lines to avoid condensation. If condensables are present, care must be taken to have instrument vents which will not become loaded with liquid and apply back pressure on the detector and sampler.

Reference Checks

In the event of doubtful analysis the use of reference standards has proved to be the best possible way to isolate the source of trouble. If the instrument checks the reference as it has previously then the sample system or process is upset. A retained master reference standard against which routine reference standards can be checked is very valuable.

Installation

The instrument should be properly installed and sheltered from the weather to avoid extreme temperature changes such as direct sun light, rain, or hail. The shelter also makes maintenance possible during extreme weather conditions and reduces instrument down time.

These are standard procedures for any analytical instrument and have evolved through experience.

Bibliography on Gas Chromatography

Prepared by a committee under the direction of

STANLEY H. LANGER AND CHARLES ZAHN

U. S. Bureau of Mines, Pittsburgh, Pennsylvania

In these proceedings, A. J. P. Martin points out, ". . . the present position of gas chromatography . . . seems to be the rapid application of well-known methods to an infinity of problems." The scope of this Bibliography lends credence to this statement. An examination of the references over the years 1952 through 1957 indicates a phenomenal increase in published material relating to the technique. It might be anticipated that one year hence, i.e., by the end of 1958, the number of articles which have appeared will have doubled the number referred to in this Bibliography. However, the references included here should be of great value to those working in the field for a number of years.

Chemical Abstracts (December, 1956) abbreviations have been used for the names of journals listed in this Bibliography. A number of general principles for the purpose of editing this Bibliography have been employed. In spite of this, for several cases the justification for including or excluding certain references is probably arbitrary.

References in trade journals and news reports referring to scientific articles or developments have not been included if they do not contribute new information of scientific value.

The titles of papers presented at national meetings of various scientific societies have been included if they have not been published to date. Where titles are accessible, papers presented at regional meetings have been included if these papers do not seem to have been published or presented at national meetings. Justification for this is the fact that these titles give important information about present workers in the field and areas under investigation.

Most references to thermal conductivity techniques not directly connected with gas chromatography have been eliminated, since these may be obtained along with other key references by referring to the published books on the technique.

Along these same lines, a number of theoretical articles on chromatography and related subjects have not been included if they did not refer specifically to gas chromatography. It is felt that the interested individual would be led directly to these through primary references.

Where it was possible, complete pagination is included rather than a reference to the initial page, since such information may be helpful.

Referee Group: D. H. Desty, Kenneth Hughes, A. I. M. Keulemans, Courtenay Phillips, Donald Rose, L. W. Safranski, Vincent J. Coates

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APPENDIX I

Standard Nomenclature Considerations and Recommendations

The Committee on Nomenclature strongly endorses the Nomenclature Recommendations of the London Symposium (1956)[1] with the following additional recommendations.

STANDARD STATIONARY PHASES

It would be of great service for an American Chemical Supply Company to follow the lead of May and Baker, and British Drug Houses in furnishing standard liquid phases as mentioned in the London Nomenclature Recommendations. There should be cooperation between the American and British firms to insure adherence to a standard, "chromatographic grade" purity. If necessary, they should obtain their materials from a common source.

RETENTION VALUES

It was felt that allowable temperature variations, rather than temperature control techniques, should be specified in the obtaining of relative and absolute retention volumes. Specifically, the temperature along the length of the column should be held constant to better than ±0.5°C for the length of the run, while obtaining relative retention volumes. For absolute measurements, temperature control to better than ±0.1°C. is required, and information as to variation of temperature with position and time should be included. Other column parameters should be controlled to an equivalent degree.

COLUMN EFFICIENCY

There is presently some confusion as to the usage of terms such as efficiency, resolution, per cent resolution, and separation. Two terms were agreed upon as being suitable as standard nomenclature. They are (refer to Fig. 1):

a) Separation factor—the ratio of corrected retention volumes of two components, that is

$$\alpha_{xy} = \frac{t_y - t_a}{t_x - t_a}.$$

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[1] Desty, D. H., ed., "Vapour Phase Chromatography." Academic Press, New York, 1957.

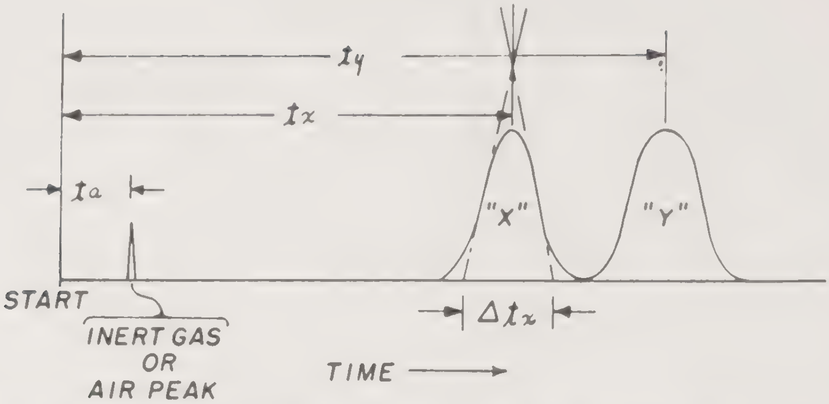

FIG. 1. Terms used in calculating column efficiency and performance.

b) Number of theoretical plates, which is defined by the Nomenclature Committee of the London Symposium as

$$r_x = 16\left(\frac{t_x}{\Delta t_x}\right)^2.$$

It should be noted that a theoretical plate is an abstract term with no physical significance other than as a measure of the relative variance of a peak. Both of these quantities are directly related to physical and chemical phenomena and are therefore considered basic.

It was also agreed that the term resolution be used in reference to the degree to which one component is freed of another. In accordance with this, it was thought the third section of nomenclature recommendations of the London Symposium could better be titled "Column Efficiency" rather than "Column Resolution." No exact definition of resolution was agreed upon. The equations and nomagraphs presented by Dr. Glueckauf[2] appear best suited as working definitions, since they combine separation factor and number of theoretical plates to determine per cent purity. However, it appears that the separation factor here used should be based on the ratio of uncorrected, rather than corrected retention times. This factor

$$B = ((t_y - t_x)/t_x)$$

has previously been used by Dr. A. J. P. Martin in his equations.

An alternate definition of resolution, the ratio of the distance between peak maxima to the width of the first peak, $((t_y - t_x)/\Delta t_x)$ was proposed by Dr. Golay. It was also pointed out that there are other methods of measuring peak width than by measuring the distance between intercepts of the inflection tangents. One such method is to measure peak width at half height. These approaches can be used, if suitable correction coefficients are added. However, it was decided to recommend the intercept method as standard nomenclature, in agreement with the nomenclature recommendations of the London Symposium.

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[2] See Keulemans, A. I. M., "Gas Chromatography," Chapter 4, pp. 96–129. Reinhold, New York, 1957.

OTHER TERMS RELATING TO COLUMN PERFORMANCE

Two other terms were felt to merit further study. They are:

c) Relative band width, R.B.W. $= \dfrac{\Delta t_x}{t_x - t_a}$,

d) Performance index,[3] P.I. $= \dfrac{(\Delta t_x)^4}{t_x^3} \cdot \dfrac{t_a \Delta P}{t_x - {}^{15}\!/\!_{16}\, t_a}$, where P is the pressure drop across the column.

However, for the present, separation factor and number of theoretical plates are regarded as the best forms of data presentation.

August 30, 1957

Walter L. Jones, Chairman
S. Dal Nogare
D. H. Desty
M. J. E. Golay
A. I. M. Keulemans
A. J. P. Martin
S. Ober
C. S. G. Phillips
J. Thoburn
E. Williams

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[3] The original, Golay, M. J. E., A performance index for gas chromatographic columns, *Nature* **180**, 435 (1957), has been modified to comply with nomenclature adopted here and also to incorporate the factor 15/16 (instead of 3/4) in accordance with theoretical findings to be published later.

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